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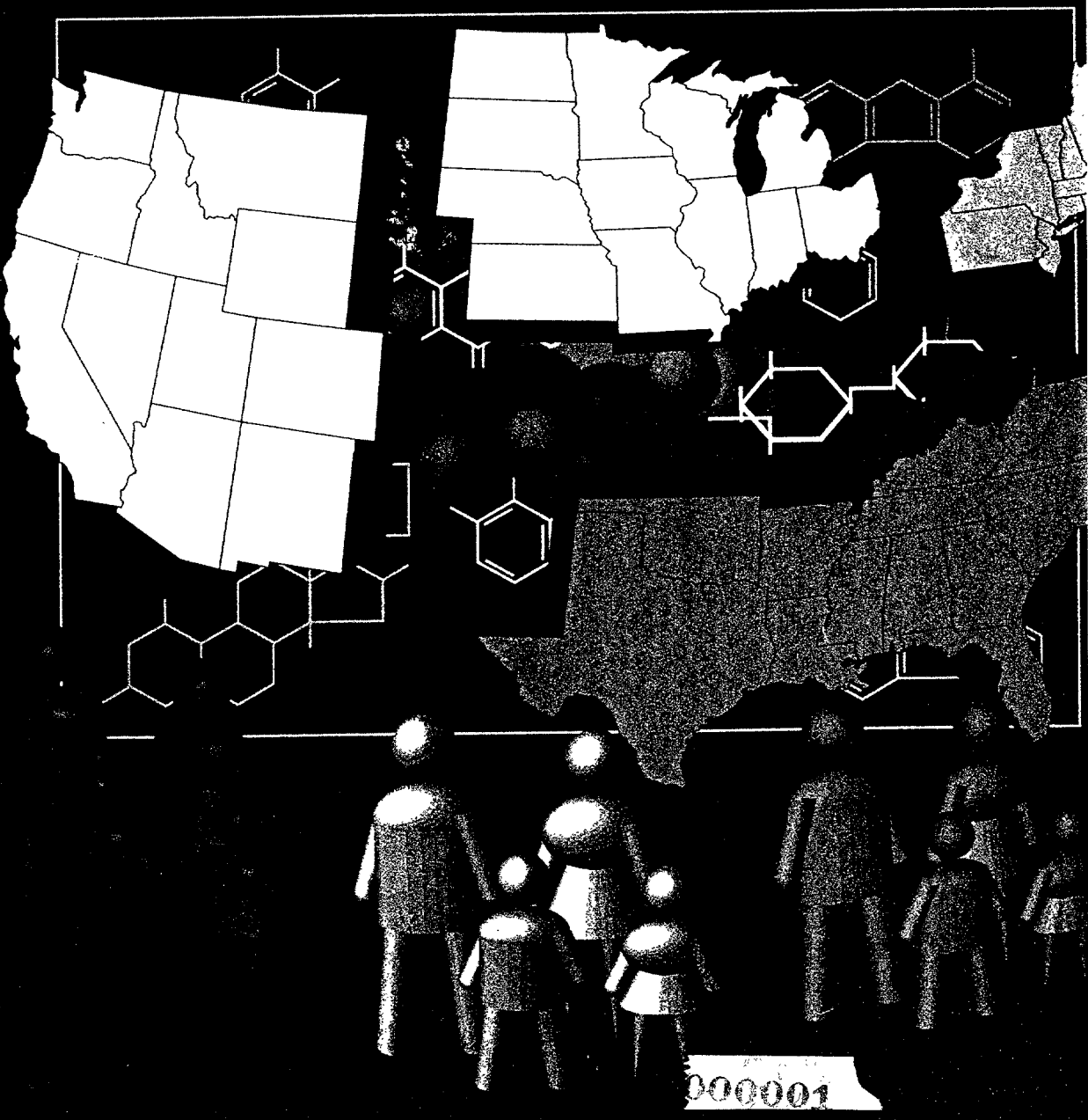
SEMIVOLATILE ORGANIC COMPOUNDS IN THE GENERAL U.S. POPULATION: NHATS FY86 RESULTS

VOLUME I



SEMIVOLATILE ORGANIC COMPOUNDS IN THE GENERAL U.S. POPULATION: NHATS FY86 RESULTS

VOLUME I

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PREFACE

The determination of the levels of semivolatile organic compounds in the general population of the United States described in this report was achieved through cooperative efforts of many EPA and contract support staff. EPA staff participating in the program included principal investigators from the Technical Programs Branch (TPB) of the Chemical Management Division (CMD) of the Office of Pollution Prevention and Toxics (OPPT). Contract support to OPPT was provided by:

- Battelle under EPA Contract Nos. 68-02-4294, 68-D8-0115, 68-D0-0126, and 68-D2-0139.
- Midwest Research Institute (MRI) under EPA Contract No. 68-02-4252.
- Westat, Inc., under EPA Contract Nos. 68-02-4293 and 68-D9-0174.

The roles and responsibilities of each of these organizations and key individuals participating in this effort are presented below.

Battelle

Battelle was responsible for developing the FY86 NHATS specimen collection program, creating and maintaining the data bases on the Patient Summary Reports, designing the specimen compositing plan and the statistical methodology for data analysis, conducting the statistical analysis to develop estimates of semivolatile residual levels in the general U.S. population based on demographic factors, and producing this final report. Key individuals included: Dr. Robert Lordo, Dr. John Orban, Mr. Ying-Liang Chou, Ms. Pamela Hartford, and Ms. Tamara Collins.

Midwest Research Institute (MRI)

MRI was responsible for the coordination of the collection of the FY86 NHATS specimens, preparation of the NHATS composites and quality control (QC) samples, conducting the HRGC/MS analysis of the composites, reporting the results, and contributing to this final report. Key individuals included: Dr. John Stanley, Dr. Stan Spurlin, Mr. Jack Balsinger, Ms. Hope Green, and Ms. Patti Alm.

Westat, Inc.

Westat was responsible for creating and maintaining the data bases for the Analysis Reports, developing and executing statistical procedures for identifying outliers in the reported concentrations, and writing the final report on the results of the outlier analysis. Key individuals included: Mr. John Rogers and Ms. Helen Powell.

EPA/OPPT

EPA/OPPT was responsible for oversight in the development of the study plan, managing and coordinating the conduct of the overall study, and reviewing, editing and finalization of this report. Key individuals included: Dr. Khoan Dinh, Ms. Janet Remmers, and Mr. John Schwemberger as Work Assignment Managers and Dr. Joseph Breen, Ms. Edith Sterrett, Mr. Gary Grindstaff, and Mr. Philip Robinson as Project Officers.

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EXECUTIVE SUMMARY

BACKGROUND

The National Human Monitoring Program (NHMP), operated by the United States Environmental Protection Agency's Office of Pollution Prevention and Toxics (USEPA/OPPT), is a national program to monitor the human body burden of selected chemicals. The National Human Adipose Tissue Survey (NHATS), one component of the NHMP, was performed annually to collect and analyze a nationwide sample of adipose tissue specimens from autopsied cadavers and surgical patients. The purpose of the NHATS was to identify and quantify the prevalence and levels of selected chemicals in human adipose tissue. The analysis results were used to establish an exposure-based chemicals list, to estimate baseline body burden levels for selected chemicals, and to characterize trends in these levels within predefined demographic groups. The NHATS was intended to fulfill the human and environmental monitoring mandates of the Toxic Substances Control Act and the Federal Insecticide, Fungicide, and Rodenticide Act, as amended.

The EPA/OPPT earmarked the FY86 NHATS tissue repository for the analysis of semivolatile compounds using HRGC/MS methods. The FY86 NHATS study design was similar to those used in the FY82 and FY84 NHATS, where HRGC/MS analyses of semivolatile compounds were also performed. This report presents the objectives, methodology, and results of the FY86 NHATS, and a comparison of results with the FY82 and FY84 NHATS.

OBJECTIVES

The specific objectives of the FY86 NHATS analysis were to:

- Determine the extent to which semivolatile organic compounds are present in human adipose tissue samples,

- Estimate the average concentrations of semivolatiles in the adipose tissue of humans in the U.S. population and in its various subpopulations,

- Determine if any key demographic factors (geographic region, age, race, and sex) are associated with the average concentrations of semivolatiles in human adipose tissue, and

- Compare the estimated average concentration levels of semivolatiles in the FY86 NHATS with estimates from the FY82 and FY84 NHATS, when similar techniques were used to estimate the same semivolatiles.

APPROACH

One hundred and eleven (111) qualitative and quantitative semivolatile organic compounds were targeted in the chemical analysis of human adipose tissue samples in the FY86 NHATS. For compounds with sufficient detection percentages, measured concentration data were statistically analyzed to estimate average concentration levels in the U.S. population and to determine if any of four demographic factors of interest (geographic region, age, race, and sex) were associated with the average concentration levels. Statistical analysis was also used to compare average concentration levels found in the FY82, FY84, and FY86 NHATS for selected compounds.

The analytical samples in the FY82, FY84, and FY86 NHATS were composites of individual patient specimens. Compositing criteria were established to achieve the study objectives of estimating and comparing average concentrations in selected subpopulations, while reducing the number of samples to analyze. The criteria specified that composites should only be created using specimens from donors in the same age group and from the same U.S. Census division. This ensured maximum precision for estimating differences in body burden levels among populations from different geographic regions and age groups.

A total of 50 composite samples were analyzed in the FY86 NHATS. These samples were prepared from 671 individual

collected from selected metropolitan statistical areas in the 48 conterminous United States.

OF THE FY86 NHATS RESULTS

Of the 111 semivolatiles targeted for analysis, 23 were in at least half of the FY86 NHATS composite samples. compounds and their detection percentages among the FY86 composite samples are listed in Table ES-1. For tive purposes, this table also includes the detection ges for these compounds among the FY82 and FY84 NHATS site samples. Seventeen (17) of the compounds in Table ES-1 lected for statistical analysis of measured concentrations FY86 NHATS.

Concentration estimates for the five PCB homologs ded in Table ES-1 (tetra-, penta-, hexa-, hepta-, and octa- obiphenyl) were consolidated to characterize overall PCB ures. The following additional PCB parameters were lated from these five homologs and presented with the study ults:

- Total concentration of PCBs (sum of the estimated concentrations of the five homologs);
- Chlorobiphenyl distribution (percentage of total PCB concentration attributed to a specific homolog);
- Chlorination level (sum of the chlorobiphenyl distribution percentages across homologs, each weighted by the homolog's chlorine mass fraction).

that these PCB parameters should be calculated across all PCB homologs. However, since each omitted homolog was ected in no more than 30% of the FY86 composite samples, the meter estimates closely approximate results across all ologs.

ional Average Concentrations

Table ES-2 contains the model-based estimates of the 86 national average concentrations in human adipose tissue for

Table ES-1. Semivolatile Compounds Detected in at Least 44% of the FY86 NHATS Composite Samples

Compound	CAS Number	Detection Percentage FY82	FY84	FY86
Pesticides				
p,p-DDE	72-55-9	100%	96%	100%
p,p-DDT	50-29-3	68%	89%	96%
Heptachlor epoxide	1024-57-3	70%	80%	94%
Beta-BHC	319-85-7	93%	89%	92%
Trans-nonachlor	39765-80-5	57%	96%	92%
Oxychlordane	26880-48-8	--	83%	78%
Dieldrin[1]	60-57-1	33%	39%	62%
Chlorobenzenes				
Hexachlorobenzene	118-74-1	79%	83%	98%
1,4-Dichlorobenzene	106-46-7	--	--	86%
PAHs				
Naphthalene	91-20-3	42%	24%	84%
PCBs				
Hexachlorobiphenyl	26601-64-9	75%	98%	94%
Pentachlorobiphenyl	25429-29-2	73%	85%	88%
Heptachlorobiphenyl	28655-71-2	52%	84%	86%
Tetrachlorobiphenyl	26914-33-0	55%	41%	66%
Octachlorobiphenyl	31472-83-0	41%	18%	44%
Phthalate Esters				
Bis (2-ethylhexyl) phthalate[2]	177-81-7	--	0%	78%
Di-n-butyl phthalate[2]	84-74-2	50%	100%	76%
Butyl benzyl phthalate[2]	85-68-7	74%	62%	72%

Table ES-1. (cont.)

	CAS Number	Detection Percentage FY82	FY84	FY86
Other (Quantitative)				
[illegible]nane[2]	5898-27-5	--	--	96%
[illegible]ane[2]	527-84-4	--	--	80%
[illegible]thyl-[illegible]cyclotetrasiloxane[2]	556-67-2	--	--	72%
Other (Qualitative)				
[illegible]l acetate	142-92-7	--	--	82%
[illegible]-Trimethylbenzene[2]	95-63-6	--	--	62%
[illegible]ene	124-11-8	--	--	50%

[illegible]ata qualifier in FY86 determined to reflect the S/N ratio had data [illegible]een above the lowest calibration standard.
Potential contamination issues with these compounds prevented them [illegible]rom being included in FY86 statistical analysis.

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Table ES-2. Estimates of National Average Concentrations for Selected Semivolatiles, With 95% Confidence Intervals, from the FY86 NHATS

Compound	Estimated Avg. Conc. (ng/g)	95% Confidence Interval
Pesticides		
p,p-DDT	177.	(137., 217.)
p,p-DDE	2340.	(1790., 2880.)
Beta-BHC	157.	(107., 207.)
Heptachlor epoxide	57.6	(49.2, 66.1)
Oxychlordane	114.	(98.4, 129.)
Trans-nonachlor	130.	(99.6, 161.)
Dieldrin	47.0	(31.0, 63.1)
Chlorobenzenes		
1,4-Dichlorobenzene	90.9	(60.2, 122.)
Hexachlorobenzene	51.3	(43.3, 59.3)
PAHs		
Naphthalene	20.7	(15.9, 25.4)
PCBs		
Tetrachlorobiphenyl	56.4	(46.9, 65.9)
Pentachlorobiphenyl	135.	(104., 165.)
Hexachlorobiphenyl	314.	(276., 351.)
Heptachlorobiphenyl	125.	(80.7, 169.)
Octachlorobiphenyl	42.7	(19.3, 66.1)
Total PCBs[1]	672.	(603. , 742.)
Level of Chlorination[2]	58.3%	(51.2, 65.4)
Other (Qualitative)		
1-Nonene	124.	(20.6, 227.)
Hexyl acetate	123.	(79.5, 166.)

Table ES-2

imate for Total PCBs is the sum of the estimated averages over the mologs included in this table (i.e., homologs detected in at least the NHATS FY86 composite samples).

ted level of chlorination is calculated as follows:

$$\sum_{i=4}^{8} (A_i * B_i) \quad ,$$

A_i = estimate of the percent of total PCBs for homolog i,
B_i = mass fraction of chlorine for homolog i.
the five PCB homologs included in the table are considered in culating level of chlorination.)

the 17 compounds included in the statistical analysis. Approximate 95% confidence intervals are included in this table for each national average. Relative standard errors of these estimates ranged from 5.9% for hexachlorobiphenyl to 27.1% for octachlorobiphenyl.

Age Group Effects

The effect of age group on average concentration for the 17 compounds in Table ES-2 was statistically significant for six of the seven pesticides (all except dieldrin), five PCB homologs, and hexachlorobenzene. In each case, the average concentration increased with the age of the donor. Among the PCB homologs, the average concentration for the 45+ age group was from 188% (pentachlorobiphenyl) to 706% (heptachlorobiphenyl) above the average for the 0-14 age group (an increase from 75.6 to 218 ng/g for pentachlorobiphenyl, and from 26.9 to 217 ng/g for heptachlorobiphenyl). Similar percent increases were observed with the pesticides. For example, average concentration of p,p-DDT was 73 ng/g for the 0-14 age group and 252 ng/g for the 45+ age group -- a 245% increase.

Geographic Effects

Statistically significant differences in average concentration for the 17 compounds in Table ES-2 were observed between census regions for p,p-DDT, p,p-DDE, heptachlor epoxide, hexachlorobenzene, naphthalene, and three of the five PCB homologs. Average concentration of p,p-DDT and the PCBs were highest in the northeast. Heptachlor epoxide was highest in the south, and hexachlorobenzene was highest in the west. Similar such patterns were observed in the FY82 and FY84 NHATS.

Race and Sex Groups

The differences in estimated average concentrations between race groups (white vs. nonwhite) and between sex groups

(male vs. female) were not statistically significant for any of the 17 modeled compounds.

SUMMARY OF THE COMPARISON WITH FY82 AND FY84 NHATS RESULTS

Fifty-four (54) of the 111 semivolatiles analyzed in the FY86 NHATS were also analyzed in either one or both of the FY82 or FY84 NHATS. Of these 54 compounds, twelve were detected in at least 50% of the samples in each of the FY82, FY84, and FY86 surveys. Statistical comparison of average concentration across surveys was performed on ten of these twelve compounds (butyl benzyl phthalate and di-n-butyl phthalate were excluded from statistical analysis based on FY86 QC data analysis findings). The estimated national average concentrations within each survey for these ten compounds, along with approximate 95% confidence intervals, are listed in Table ES-3. Statistical analysis results are also included in Table ES-3 to identify those compounds whose results for FY82 and FY84 differ significantly from FY86.

For the four PCB homologs considered in the statistical comparison, the FY86 average concentration was from 48% to 259% higher than the FY82 average concentration. The differences in these averages for tetra-, penta-, and hexa-chlorobiphenyl were statistically significant between these two surveys. The observed differences in average concentration for PCB homologs between FY84 and FY86 were less apparent; the only statistically significant difference was a 58% increase from FY84 to FY86 in average concentration for hexachlorobiphenyl. Total PCBs in FY82 and FY84 differed significantly from FY86 results, due to the larger national average noted in FY86.

Fewer incidents of significant differences between surveys were apparent among the five pesticides. For p,p-DDT and p,p-DDE, differences of 43% and 101%, respectively, between the FY84 and FY86 average concentrations were statistically significant. Both differences were increases over the FY84 average. Meanwhile, the only pesticide with a significant

Table ES-3. Estimates of National Average Concentrations for Selected Semivolatiles, With 95% Confidence Intervals, from the FY82, FY84, and FY86 NHATS

Compound	NHATS	Estimated Avg. Conc. (ng/g)	95% Confidence Interval	Diff. From FY86
		Pesticides		
p,p-DDT	FY82	189.	(125., 253.)	12.1
	FY84	123.	(102., 145.)	-53.4*
	FY86	177.	(137., 217.)	
p,p-DDE	FY82	1840.	(1130., 2550.)	-498.
	FY84	1150.	(968., 1330.)	-1190.*
	FY86	2340.	(1790., 2880.)	
Beta-BHC	FY82	291.	(183., 400.)	135.*
	FY84	199.	(150., 248.)	42.3
	FY86	157.	(107., 207.)	
Trans-nonachlor	FY82	109.	(53.0, 165.)	-21.3
	FY84	105.	(94.4, 115.)	-25.8
	FY86	130.	(99.6, 161.)	
Heptachlor epoxide	FY82	59.4	(32.2, 86.5)	1.73
	FY84	68.3	(53.9, 82.6)	10.6
	FY86	57.6	(49.2, 66.1)	
		Chlorobenzenes		
Hexachlorobenzene	FY82	118.	(1.0, 256.)	66.9
	FY84	42.9	(31.9, 53.9)	-8.38
	FY86	51.3	(43.3, 59.3)	
		PCBs		
Tetrachlorobiphenyl	FY82	15.7	(12.8, 18.6)	-40.7*
	FY84	48.8	(36.8, 60.8)	-7.60
	FY86	56.4	(46.9, 65.9)	
Pentachlorobiphenyl	FY82	78.3	(62.3, 94.4)	-56.2*
	FY84	115.	(92.8, 137.)	-19.8
	FY86	135.	(104., 165.)	
Hexachlorobiphenyl	FY82	176.	(119., 233.)	-137.*
	FY84	198.	(177., 220.)	-115.*
	FY86	314.	(276., 351.)	

Table ES-3. (cont.)

Compound	NHATS	Estimated Avg. Conc. (ng/g)	95% Confidence Interval	Diff. From FY86
	PCBs (cont.)			
Heptachlorobiphenyl	FY82	84.6	(50.1, 119.)	-40.5
	FY84	129.	(107., 149.)	3.51
	FY86	125.	(80.7, 169.)	
Total PCBs[1]	FY82	407.	(337. , 476.)	-266.*
	FY84	508.	(469. , 547.)	-164.*
	FY86	672.	(603. , 742.)	
Chlorination Level[2]	FY82	59.3%	(47.7, 71.0)	1.0
	FY84	58.1%	(53.1, 63.1)	-0.2
	FY86	58.3%	(51.2, 65.4)	

* Significantly different from zero at the 0.05 level.
(1) Sum of concentrations for tetra- to octa-chlorobiphenyl.
(2) Overall chlorination level for PCBs, defined in Section 6.2.1.2.

difference in average concentration between the FY82 and FY86 NHATS was beta-BHC; this difference was a 46% decrease from the FY82 estimate.

When interpreting the observed differences in the average concentration levels between the FY86 NHATS and both the FY82 and FY84 NHATS, it is important to consider differences in analytical approach. For example, differences in the internal quantitation standards used, the recovery levels observed, the analytical laboratories, and improvements made in the analytical method over time all may contribute substantially to observed differences between surveys.

Additional surveys under the current analytical approach (HRGC/MS on composite samples) covering a longer time period are needed to more accurately characterize and interpret trends in average concentration levels of semivolatiles. As has been done in the past, the designs and analysis methods for these surveys should be established to meet the objective of comparing results across surveys, while minimizing any nuisance effects contributing to the comparisons.

1.0. INTRODUCTION

1.1. BACKGROUND

The National Human Adipose Tissue Survey (NHATS) has been the main operative program of EPA's National Human Monitoring Program (NHMP). The NHATS program has collected and analyzed human adipose tissue samples on an annual basis to monitor human exposure to potentially toxic compounds. The NHMP/NHATS was established by the U.S. Public Health Service in 1967 and transferred to the EPA in 1970. Since 1981, the EPA Office of Pollution Prevention and Toxics (EPA/OPPT) has been responsible for the NHMP/NHATS. The NHATS intended to fulfill the human and environmental monitoring mandates of the Toxic Substances Control Act and the Federal Insecticide, Fungicide, and Rodenticide Act, as amended.

Adipose tissue specimens were collected annually for the NHATS by cooperating pathologists and medical examiners during routine post-mortem examinations or elective surgeries. These cooperators were selected from a statistical sample of Metropolitan Statistical Areas (MSAs) within the 48 conterminous United States. Target quotas specifying the number of specimens within each donor age, race, and sex classification were established for each collection center. Sampling plans were designed for each annual survey to produce statistically unbiased and precise estimates of the levels and prevalence of compounds in the U.S. population and in various demographic subpopulations.

In the 1970s and early 1980s, the NHATS program characterized the prevalence and levels of 19 organochlorine pesticides and polychlorobiphenyls (PCBs) in individual human adipose tissue specimens, using packed column gas chromatography/ electron capture detection (PGC/ECD) methods. Recognizing the need to extend the capabilities of the NHATS program, the EPA/OPPT initiated a series of programs in 1984 to expand the utility of the tissue repository. In order to expand the list of target compounds monitored by NHATS, a change to high-resolution

gas chromatography/mass spectrometry (HRGC/MS) methods was made. Individual specimens were composited prior to HRGC/MS analysis to optimize the amount of data which could be generated. Analysis on composite samples rather than individual patient samples necessitated a modified statistical analysis approach to obtain national and subpopulation estimates at an individual level.

The first study in the NHATS program which utilized the expanded capabilities of the HRGC/MS methodology was the "Broad Scan Analysis Study" (Mack and Panebianco, 1986). The FY82 NHATS specimen repository was selected for this study. The target chemicals considered in this broad scan study included 30 semivolatile compounds, 17 volatile organic compounds, and 11 polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs). The broad scan study demonstrated that 13 of these semivolatile compounds, 11 of the volatile compounds, and nine of the dioxins and furans were detected in at least half of the composite samples. Estimated average levels for some semivolatiles increased significantly with age, while the South and Northeast census regions tended to have higher levels than the West and North Central regions.

The FY84 NHATS specimen repository was used in conducting a comparability study between the PGC/ECD and HRGC/MS analytical methods (Westat, 1990). Paired composite samples were analyzed using both methods. A total of 58 semivolatile compounds were analyzed by HRGC/MS, of which 14 were detected in at least 50% of the samples. The results of the comparability study indicated that the PGC/ECD method was generally more sensitive than the HRGC/MS method in measuring concentrations for a variety of lipophilic compounds, with the opposite holding true for PCBs. Method comparability issues have yet to be resolved for many of the target semivolatile compounds.

The goal of the study performed on the NHATS FY86 specimen repository was to estimate baseline body burden levels of semivolatile organic compounds, and to characterize trends in these levels within predefined demographic groups (census region,

age group, sex, and race). HRGC/MS methods were employed so that FY86 results could be compared to FY82 and FY84 results. A total of 111 semivolatile compounds were analyzed in the FY86 NHATS. This report presents the results of the FY86 NHATS analysis on semivolatiles, along with the comparison to results from the FY82 and FY84 NHATS.

1.2. OBJECTIVES

The specific objectives of the FY86 NHATS and analysis were to:

- Determine the extent to which semivolatile organic compounds are present in human adipose tissue samples,
- Estimate the average concentrations of semivolatiles in the adipose tissue of humans in the U.S. population and in its various subpopulations,
- Determine if any key demographic factors (geographic region, age, race, and sex classification) are associated with the average concentrations of semivolatiles in human adipose tissue, and
- Compare the prevalence and estimated average concentration levels of semivolatiles in the FY86 NHATS with that from the FY82 and FY84 NHATS, where similar sampling and analytical techniques were used.

The results of this study will contribute to EPA's knowledge base on the prevalence and concentration levels of semivolatiles in human adipose tissue samples. Statistical analysis will determine the extent to which concentrations of these compounds are changing over a six-year time frame in the 1980s, relative to analytical effects and trends.

1.3. REPORT ORGANIZATION

Volume I of this report presents the methods, results, and conclusions of the statistical analysis conducted on the FY86 NHATS adipose tissue sample data. While discussions on sample design, composite design, and chemistry methods are also included

in this report, these subjects are more fully addressed in other references (see Chapter 9).

Battelle developed the sample design and composite design for the FY86 NHATS. The sample and composite designs are highlighted in Chapters 2 and 3, respectively.

Chapter 4 discusses the chemistry procedures that Midwest Research Institute (MRI) used to analyze the FY86 composite and QC samples. Included in this chapter are discussions of overall data quality, analytical procedures, and QA/QC procedures.

FY86 data issues and other pre-statistical analysis results are presented in Chapter 5. Detection status of the 111 semivolatile compounds are presented, along with data issues found to be unique to the FY86 analysis approach. For example, methods were developed in this effort to adjust measured concentrations for surrogate recoveries in order to more accurately estimate actual sample concentrations. The results of statistical analysis on QC sample data are presented in Chapter 5; these results characterize measurement error, recoveries, background levels, and the presence of batch effects.

Chapter 6 contains a discussion of the statistical methodologies used by Battelle in estimating average concentration levels and associated standard errors for target compounds. The results of applying these statistical methodologies to the FY86 NHATS data are presented in Chapter 7. Finally, Chapter 8 presents the results of comparing FY86 NHATS results with those from the FY82 and FY84 NHATS for the same compounds.

Supporting information on individual sample data, including data listings and plots, data summary statistics, QC data plots, and graphical display of the estimated average concentrations with associated levels of uncertainty, is included as appendices. These appendices constitute Volume II of this document.

2.0 NHATS FY86 SAMPLE DESIGN

The human adipose tissue specimens in the FY86 NHATS repository were collected from October, 1985, through September, 1986. The method in which these specimens were supplied to the NHATS program follows the NHATS Sampling Design. In each year of the NHATS program, cooperators (hospital pathologists or medical examiners) collected approximately 700-1200 adipose tissue specimens. Although the NHATS target population is the general, noninstitutionalized U.S. population, the sampling population was limited to cadavers and surgical patients due to the invasive nature of the process required to collect the adipose specimens from living persons.

Section 2.1 discusses the NHATS Sampling Design and its multistage characteristics. Methods used to collect specimens are discussed in Section 2.2. Finally, a summary of the types of specimens collected in the FY86 NHATS is presented in Section 2.3.

2.1 SAMPLING DESIGN

The NHATS program used a multistaged sampling design to obtain adipose tissue specimens from autopsied cadavers and surgical patients throughout the United States. The NHATS Sampling Design consisted of three components:

- The 48 conterminous states were stratified into distinct geographical areas.
- A sample of Metropolitan Statistical Areas (MSAs) was selected within the strata. The probability of selecting an MSA was proportional to its population percentage within the stratum.
- One or more cooperators were chosen from each MSA and asked to supply a specified quota of tissue specimens to the NHATS. To maintain similarity in the sampling designs across fiscal years, the same MSAs and cooperators were retained from year to year to the extent possible.

As part of the third component of the NHATS Sampling Design, the manner in which cooperators selected the donors and tissue specimens was nonprobabilistic, but followed a specific set of criteria. Quotas and subquotas for the number of specimens supplied to the NHATS were assigned to each cooperator. The subquotas determined the desired number of specimens coming from particular combinations of donor age group, race, and sex. Demographic categories in which subquotas were defined are presented in Table 2-1. The subquotas were proportional to the 1980 U.S. Census population counts for each sampling stratum.

Table 2-1. Demographic Categories in Which Subquotas Were Established for Collecting Adipose Tissue Specimens

Subquota	Categories
Age group	0-14 years 15-44 years 45+ years
Race group	Caucasian Non-Caucasian
Sex group	Female Male

Because the survey required some divergence from strict probabilistic sampling, the validity of the statistical estimates derived from the data depended on several assumptions:

- The concentrations of toxic substances in the adipose tissue of cadavers and surgical patients are assumed to be comparable to those in the general population.
- The levels of toxic substances in urban residents are approximately the same as in rural residents, and thus the selection of only urban hospitals and medical examiners (i.e., those located in MSAs) does not introduce any significant bias into the estimates of average concentration levels.

- No systematic bias is introduced by the fact that the cooperators are not randomly selected and that the donors and specimens are nonprobabilistically sampled according to pre-specified quotas.

Further discussion of the three components of the NHATS Sampling Design follow.

2.1.1 The NHATS Stratification Scheme

Prior to 1985, the sampling strata from which MSAs were randomly selected were the nine U.S. Census divisions. But in 1985, EPA wanted the ability to obtain estimates of average concentration levels in each of the ten EPA regions. Thus, beginning with the FY85 NHATS, the sampling strata were redefined as seventeen geographic areas of the country, resulting from the intersection of the nine census divisions and the ten EPA regions. Selecting the sample under this new stratification scheme made it possible to make comparisons with previous NHATS results and also obtain estimates for the EPA regions. The states, census divisions, and EPA regions that define the seventeen strata are shown in Table 2-2.

Although the FY86 NHATS sampling design specified that specimens be collected across the seventeen strata, it was not possible to create composites so that all specimens within a composite came from the same stratum. However, the Composite Design assured that each composite contained specimens originating from the same census division and age group. This was done to ensure that the FY86 and FY82 analysis results could be compared. Chapter 3 discusses the Composite Design in greater detail.

2.1.2 MSA Selection

The MSAs were the primary sampling units in the NHATS sampling plan. Cooperators were recruited from each selected MSA to provide tissue samples for the NHATS.

Table 2-2. Sampling Strata Definitions for the NHATS

Stratum	Census Division	EPA Region	States
			Texas
10	West North Central	7	Iowa Missouri Nebraska Kansas
11	West North Central	8	North Dakota South Dakota

Table 2-2. (cont.)

Stratum	Census Division	EPA Region	States
12	Mountain	8	Montana Wyoming Colorado Utah
13	Mountain	9	Arizona Nevada
14	Pacific	9	California
15	Mountain	10	Idaho
16	Pacific	10	Washington Oregon
17	Mountain	6	New Mexico

Once the seventeen sampling strata were identified for the FY85 NHATS, a sample of MSAs was selected using a controlled selection technique, known as the Keyfitz technique (Kish and Scott, 1971). This sample differed from those MSAs selected prior to the FY85 NHATS. However, the Keyfitz technique maximized the probability of retaining previously selected MSAs, thus allowing to continue employing existing cooperators (Mack, et. al., 1984). The MSA sample selected in FY85 served as the base NHATS sample for FY86 through FY91.

The FY86 NHATS sampling design contained 46 MSAs, of which two (St. Louis and Moline) were each split into two primary sampling units to reflect areas of the MSA falling into different sampling strata. All but one of the MSAs selected for the FY85 NHATS were used in the FY86 NHATS; the omitted MSA (Medford OR) was replaced (Eugene OR) because satisfactory cooperators could not be found. The sample MSAs for the FY86 NHATS are listed by stratum in Table 2-3. Four MSAs (Los Angeles, Chicago, Detroit, and New York) were listed as double collection sites because their populations were much larger than other MSAs within their strata. Strata 13, 15, and 17 had no MSAs selected due to their small population sizes.

2.1.3 Specimen Collection Quotas

Pre-assigned quotas determined the numbers of specimens selected within each sample MSA. In addition, demographic subquotas were assigned to each MSA to ensure that the specimens collected were representative of the strata with respect to the three demographic factors in Table 2-1 (age group, race group, and sex group). The subquota assigned to each MSA was determined by the demographic makeup of the stratum to which the MSA belonged and was based on the 1980 U.S. Census population counts. Each combination of age group and sex was proportionally represented in the subquota. The race categories were also proportionally represented, but the subquota did not specify that Caucasians and non-Caucasians were to be proportionally

Table 2-3. Sample MSAs Selected for the FY86 NHATS

Stratum	Census Division	EPA Region	MSAs
1	New England	1	Springfield, MA Boston, MA
2	Middle Atlantic	2	Albany, NY New York, NY(1) Binghamton/Elmira, NY Newark, NJ
3	Middle Atlantic	3	Philadelphia, PA Pittsburgh, PA Erie, PA
4	South Atlantic	3	Washington, DC Norfolk, VA
5	South Atlantic	4	Tampa, FL Greenville, SC Orlando, FL West Palm Beach/ Boca Raton, FL Miami, FL Atlanta, GA
6	East South Central	4	Memphis, TN(2) Birmingham, AL Lexington, KY
7	East North Central	5	Dayton, OH Detroit, MI(1) Columbus, OH Cleveland, OH Akron, OH Chicago, IL(1) Madison, WI Moline, IL(2)
8	West North Central	5	Rochester, MN
9	West South Central	6	El Paso, TX Lubbock, TX Houston, TX San Antonio, TX Dallas, TX
10	West North Central	7	Omaha, NE St. Louis, MO(2)

Table 2-3. (cont.)

Stratum	Census Division	EPA Region	MSAs
11	West North Central	8	Sioux Falls, SD
12	Mountain	8	Salt Lake City, UT Denver, CO
14	Pacific	9	San Francisco, CA Sacramento, CA Los Angeles, CA(1)
16	Pacific	10	Portland, OR Spokane, WA Eugene, OR(3) Yakima, WA

(1) Indicates a double collection site. A double collection site is an MSA whose population relative to its stratum is so large that its proper representation in the sample requires it to be selected twice.

(2) Indicates a split MSA. A split MSA is one which covers more than one stratum. Only the portion of the stratum in which the MSA is listed is represented in the sample.

(3) Indicates a replacement MSA. A replacement MSA is an MSA that was not selected in the FY85 probability sample, but was chosen to replace an FY85 sample MSA for which a satisfactory cooperator could not be found.

represented within each combination of age group and sex. The subquotas only specified the total number of Caucasian and non-Caucasian specimens to be collected from each MSA.

The subquotas for the seventeen sampling strata for the FY86 sample design are presented in Table 2-4. Each MSA had a quota of twenty-seven specimens, except for the four MSAs that were designated as double collection MSAs. In those MSAs, the quotas and subquotas were doubled. Cooperators within an MSA were assigned quotas and subquotas appropriate to that MSA.

The total number of samples specified for the FY86 NHATS was 1404. This was based on the quota of twenty-seven specimens for each of the forty-eight MSAs, plus twenty-seven additional specimens for each of the four MSAs designated as double collection MSAs.

2.2 SAMPLE COLLECTION PROCEDURES

NHATS specimens were adipose tissue samples excised by pathologists and medical examiners during therapeutic or elective surgery or during postmortem examinations. If the specimen was collected postmortem, the tissue was obtained from an unembalmed cadaver which had been dead for less than twenty-four hours and had been kept under refrigeration during that time. The death should have been caused by sudden traumatic injury, such as cardiac arrest, car accident, or gunshot wound.

The following groups were excluded from specimen collection:

- institutionalized individuals;
- persons known to be occupationally exposed to toxic chemicals;
- persons who died of pesticide poisoning; and
- persons suffering from cachexia.

Table 2-4. FY86 Age and Sex Subquotas, and the Race Subquota, for Each NHATS Collection Site Within Each Stratum

Stratum #	Census Division	EPA Region	# non-Caucasian	0-14 years		15-44 years		45+ years	
				M	F	M	F	M	F
1	New England	1	2	3	3	6	6	4	5
2	Middle Atlantic	2	5	3	3	6	6	4	5
3	Middle Atlantic	3	3	3	3	6	6	4	5
4	South Atlantic	3	6	3	3	6	7	4	4
5	South Atlantic	4	6	3	3	6	6	4	5
6	East South Central	4	5	3	3	6	6	4	5
7	East North Central	5	4	3	3	6	6	4	5
8	West North Central	5	1	3	3	6	6	4	5
9	West South Central	6	6	4	3	6	6	4	4
10	West North Central	7	2	3	3	6	6	4	5
11	West North Central	8	2	3	3	6	6	4	5
12	Mountain	8	2	3	3	7	7	3	4
13	Mountain	9	4	3	3	6	6	4	5
14	Pacific	9	7	3	3	6	7	4	4
15	Mountain	10	1	4	4	6	6	3	4
16	Pacific	10	2	3	3	7	7	3	4
17	Mountain	6	7	4	3	6	7	3	4

For each stratum, the six subquotas across age and sex groups add to 27, the total quota for each selected MSA from the stratum. The non-Caucasian subquota represents the number of specimens out of 27 corresponding to non-Caucasian donors.

These guidelines were stipulated so that the levels of substances detected in the specimens were a result of environmental exposure.

Instructions for the cooperators stipulated that at least five grams of tissue be obtained from each donor. In addition, the cooperators were to avoid contamination through contact with disinfectants, paraffins, plastics, preservatives, and solvents. Cooperators placed the collected specimens in glass jars with Teflon® lids and stored them at -10° to -20° C. The jars were packed on dry ice for overnight shipment to MRI, the contractor responsible for tissue storage. MRI received the specimens and checked them for adequacy of shipping conditions and level of conformance with cooperator quota. MRI determined an approximate specimen weight and transferred the specimens to storage at -20° C. Upon examining the patient summary reports, MRI forwarded the reports to Battelle for processing.

2.3 SPECIMEN COLLECTION SUMMARY

In the FY86 NHATS, cooperators provided 739 specimens in 31 of the sample MSAs. In preliminary review of the specimens, 671 were collected in accordance with the quotas and subquotas. These specimens were labeled "Design" specimens. The remaining specimens were labeled "Surplus" specimens, as their collection was considered beyond the quotas and subquotas requested.

The process of labeling specimens as Design or Surplus followed established guidelines (Orban, et. al., 1988). However, EPA added a stipulation that the collection dates of Surplus specimens be uniformly distributed throughout the fiscal year. Also, it was necessary to modify Surplus specimen assignment from the preliminary review, as one composite contained mostly low weight specimens. Surplus specimens were relabeled as Design specimens and added to this composite in order for the composite to achieve sufficient tissue mass. Meanwhile, the same number of Design specimens from another amply-represented composite within the same census division were relabeled Surplus specimens and

removed from the composite. Thus the total number of Surplus specimens collected in FY86 did not change following this adjustment. The maximum number of specimens from a MSA remained at the original quota of twenty-seven (or fifty-four from a double-collection MSA)

Table 2-5 is a summary of the collection effort for the FY86 NHATS, detailed by census division. In FY86, EPA chose not to make estimates for EPA regions. Instead, EPA maintained similarity to the FY82 geographic classifications in order to compare FY86 results to FY82 results. All 671 Design specimens were placed into one of fifty composites, on which laboratory analysis was performed.

Table 2-6 shows the number of quota specimens, collected specimens, and Design specimens in each of the four demographic subpopulations (census region, age group, sex, and race) which act as analysis factors in the linear model. Because the number of samples in the chemical analysis was not large enough to obtain reliable estimates for all nine census divisions, Battelle combined the divisions into four census regions for the FY82, FY84, and FY86 model analyses.

Table 2-5. FY86 NHATS Specimen Collection Summary

Census Division	No. of Design MSAs	No. of Quota Specimens	No. of Cooperating MSAs	No. of Specimens Collected	No. of Design Specimens(1)	No. of Composite Samples
New England	2	54	2	43	43	4
Middle Atlantic	7(2)	216	4(2)	81	80	5
South Atlantic	8	216	6	173	128	8
East South Central	4	108	2	51	50	4
West South Central	5	135	1	31	27	3
East North Central	8(3)	270	7(3)	209	194	11
West North Central	5	135	2	56	54	5
Mountain	2	54	2	34	34	4
Pacific	7(2)	216	5(2)	61	61	6
Total	48	1404	31	739	671	50

(1) Resulting after the Design/Surplus Indicator was assigned to each specimen.
(2) Includes one double collection quota MSA.
(3) Includes two double collection quota MSAs.

Table 2-6. FY86 NHATS Specimen Collection Summary by Demographic Subpopulation

Analysis Factor	Category	No. of Quota Specimens	No. of Specimens Collected	No. of Design Specimens
Census Region	Northeast	270	124	123
	North Central	405	265	248
	South	459	255	205
	West	270	95	95
	Total	**1404**	**739**	**671**
Age Group	0-14 years	317	115	108
	15-44 years	642	248	221
	45+ years	445	376	342
	Total	**1404**	**739**	**671**
Sex Group	Male	681	354	315
	Female	723	385	356
	Total	**1404**	**739**	**671**
Race Group	White	1179	564	529
	Nonwhite	225	175	142
	Total	**1404**	**739**	**671**

3.0 NHATS FY86 COMPOSITE DESIGN

Battelle assigned the 671 Design specimens in the FY86 NHATS tissue repository to composite samples using specific composite design criteria (Orban, et. al. 1988). The necessity for compositing samples prior to chemical analysis was to ensure that at least twenty grams of tissue were available per sample to meet the limit of detection goals for the target compounds. The Composite Design resulted in constructing 50 composite samples.

3.1 DESIGN GOALS AND COMPOSITING CRITERIA

The five goals of the FY86 NHATS Composite Design, listed in order of importance, were to:

- maintain similarity to the FY82 Composite Design,
- maintain equal weighing of specimens within the composite samples,
- specify additional numbers of pure sex composite samples than in FY82,
- control the MSA effect, and
- provide the best range of race group percentages across the composite samples.

Because of the constraints imposed by the sampling and compositing protocols and the frequency of collection nonresponse, it was not always possible to meet all the design goals. Each of the above goals required a different mix of individual specimens within the composite samples. Thus, attempts were made to achieve all goals across the design to the extent possible. The five goals are discussed in detail below.

1. Similarity to the FY82 Composite Design

EPA imposed this criterion to ensure that the results of FY86 data analysis could be compared with FY82 results, where compositing was performed and the same semivolatile compounds were analyzed. The design criterion imposed by this objective is

that each composite sample had to be constructed from individual specimens collected from exactly one census division and exactly one age group category. Thus there were 27 distinct categories within which composite samples were formed.

Once the FY86 Composite Design was established, it was desired to compare results of data analysis on the FY86 samples with the results obtained from the HRGC/MS analysis on FY84 composite samples. The FY84 Composite Design closely paralleled the FY82 Composite Design, allowing the FY86 results to be compared with the FY84 results as well as the FY82 results. Of primary importance, the FY84 design stipulated that all specimens found in a given composite originate from the same age group and census division.

2. Equal weighing of specimens within the composite samples

This criterion is primarily for ease of interpretation. In attempting to make inferences on individual specimen concentrations, it is far easier to interpret the observed composite sample concentrations as the arithmetic average of the individual specimen concentrations. Therefore, this design goal specified that each individual specimen within a composite sample contribute an equal amount of tissue to the composite sample. This specification allows the lipid-adjusted concentration of the composite sample to be interpreted as approximately the arithmetic average of the lipid-adjusted individual specimen concentrations, with equality occurring whenever all specimens in the composite sample have the same percentage of lipid material.

In the FY86 analysis, specimens were not labeled as Surplus as a result of specimen weight, nor was specimen weight used to determine whether the specimen would be included in a composite sample. The specimen weights were evaluated only after composites were defined based on the other design criteria. Composites with insufficient tissue mass for chemical analysis were modified if practical alternatives were available. This

policy resulted in combining two initial composites and modifying an additional two composites.

To ensure that equal weighing of specimens within the composite samples was maintained throughout the analysis, instructions for evaluating individual specimen weights were based on the ratio of the maximum weight to the minimum weight of all specimens within the composite sample. Any low-weight specimens causing this ratio to exceed 3.0 was recommended for removal from the composite.

3. Construct more pure sex composite samples than in FY82

Pure sex composites (composites containing specimens originating from either all male patients or all female patients) were constructed when sufficient numbers of specimens were available within a particular census division/age group category and more than one composite sample was allocated to this category by the design. Pure sex composites were needed to achieve more precise estimates of sex effects in the population. This design strategy was in contrast to the FY82 Composite Design, which provided for more balanced sex composite samples (samples with nearly half male and half female specimens). Including more pure sex composites in the FY86 design intended to reduce the standard errors for the sex group estimates from that observed for the FY82 analysis (Draper and Smith, 1981, pp. 52-55).

4. Control the MSA effect

Controlling the number of MSAs contributing specimens to composite samples was intended to reduce the effect of the MSA on the estimated average concentrations. This was done because MSAs are regarded as being major sources of differences in observed concentrations across the nation due to their varied exposure scenarios (Panebianco, 1986). To avoid confounding the MSA effect with any of the geographic or demographic effects, the Composite Design stipulated:

4a. to keep the number of MSAs represented in each composite sample consistent across the design (targeted at 2-3 MSAs), and

4b. to maintain approximately the same number of pure sex composite samples within a group of MSAs.

Criterion 4a helped to ensure a constant variance of measured concentrations across the sample whenever the composite sample concentrations are averages over an equal number of MSAs. Criterion 4b was intended to prevent confounding a large MSA effect with the sex effect.

5. Control the race group percentages across the composite samples

The benefits for constructing pure race group composite samples paralleled the benefits for constructing pure sex composite samples. **However, achieving this design goal was** dependent on the number of non-Caucasian specimens collected in the twenty-seven census division/age group categories and the number of composite samples in the design. At least one pure Caucasian composite sample and at least one pure non-Caucasian composite sample were constructed in four different census division/age group categories.

3.2 LABORATORY COMPOSITING PROCEDURES

In the FY86 NHATS Composite Design, specimens from nine census divisions and three age groups were segregated into 50 composites. Battelle provided MRI with composite sample data sheets that identified the specific individual specimens to be included in each composite (Appendix A of Orban, et. al., 1988). A composite consisted of from three to twenty-four specimens. The composite sample data sheets provided sufficient information (EPA ID number, package number, sample weight, hospital code, etc.) such that the individual specimens could be cross-checked with the study design. **The data sheets were used as work sheets** to record actual laboratory compositing procedures.

Initially, the samples were grouped into composites, and any samples of insufficient weight (< 1.0 g) or potentially contaminated samples were reported by MRI to the EPA Work Assignment Manager (WAM). Such samples were omitted from the analysis.

The weights of composites included in laboratory analysis ranged from 1.884g to 22.514g, with three composites below the target weight of 20g. The composite with the lowest weight consisted of only three samples from the 0-14 year age category. The other two composites below the target weight had insufficient samples.

The composite samples were placed on dry ice during the compositing procedure. An electronic four-place balance was used to weigh the samples, and the calibration of the balance was checked with a Class P set of weights (laboratory grade, tolerance 1/25,000) before any weighing was begun and once during the sample weighings.

To weigh the samples, a clean culture tube was labeled with the composite number. This tube was placed on the balance, and the weight was tared. A sample was removed from the composite bag, the jar opened, and a portion of the frozen adipose removed with a clean stainless steel spatula. The adipose was placed in the culture tube and the weight recorded to three decimal places on the compositing sheets. Additional adipose was added if necessary. A goal of ±10% of the desired weight was attempted where possible. The weights of the individual specimens were recorded on the composite data sheets.

The weight of the culture, beaker, and adipose tissue was rezeroed, and the next sample in the composite was weighed. A new spatula was used between each sample. This procedure was repeated for each sample in the composite. When the composite was completed, it was capped and stored in a sample freezer at -10° C. All data on the actual compositing procedures (amount added, remaining spec. weight, date inventoried, and total weight of the composite) were recorded on the data sheets provided by

Battelle. MRI submitted all data sheets in a separate report documenting the compositing activity (MRI, 1988a).

3.3 SUMMARY OF FY86 NHATS COMPOSITE SAMPLES

The FY86 NHATS Composite Design resulted in constructing 50 composite samples using 671 individual specimens collected from 31 MSAs. Composite samples were formed from specimens collected exclusively from the same census division/age group category. The numbers of composites within each of these categories are given in Table 3-1. Unlike the exclusivity by census division and age group, the composite samples had specimen percentages within sex and race groups which varied across the design depending on the availability of specimens within specific demographic subpopulations. Table 3-2 shows the demographic makeup of the FY86 NHATS composite samples.

The 50 composite samples were randomly assigned to five laboratory batches of ten samples each. Within each batch, the ten composite samples and three lipid-based QC samples were placed in random order for chemical analysis.

Table 3-1. Distribution of FY86 NHATS Composite Samples by Census Division and Age Group

Census Division	# Composites by Age Group			Total # of Composites
	0-14 years	15-44 years	45+ years	
New England	1	1	2	4
Middle Atlantic	1	2	2	5
South Atlantic	2	3	3	8
East South Central	1	2	1	4
West South Central	1	1	1	3
East North Central	1	3	7	1
West North Central	1	2	2	5
Mountain	1	1	2	4
Pacific	1	1	4	6
Total	10	16	24	50

Table 3-2. Demographic Makeup of FY86 NHATS Composite Samples

Census Division	Composite ID	Age Group[1]	Number of Individual Specimens	Number of MSAs	Percent Male	Percent Caucasian	Proportionate Tissue Amt.[2] (g)
New England	ACS8600261	1	9	2	44.4	88.9	2.22
	ACS8600270	2	13	2	53.8	69.2	1.54
	ACS8600289	3	9	2	100.0	66.7	2.22
	ACS8600298	3	12	2	0.0	100.0	1.67
Middle Atlantic	ACS8600172	1	9	3	44.4	88.9	2.22
	ACS8600181	2	21	4	100.0	85.7	0.95
	ACS8600190	2	16	3	0.0	75.0	1.25
	ACS8600207	3	18	4	100.0	88.9	1.11
	ACS8600216	3	16	4	0.0	75.0	1.25
South Atlantic	ACS8600369	1	15	6	100.0	46.7	1.33
	ACS8600378	1	12	4	0.0	58.3	1.67
	ACS8600387	2	23	4	100.0	100.0	0.87
	ACS8600396	2	16	5	43.8	0.0	1.25
	ACS8600403	2	12	4	0.0	100.0	1.67
	ACS8600412	3	15	5	100.0	100.0	1.33
	ACS8600421	3	20	6	0.0	100.0	1.00
	ACS8600430	3	15	5	33.3	0.0	1.33
East South Central	ACS8600136	1	10	2	50.0	50.0	2.00
	ACS8600145	2	9	2	100.0	77.8	2.22
	ACS8600154	2	13	2	0.0	92.2	1.54
	ACS8600163	3	18	2	44.4	72.2	1.11

Table 3-2. (cont.)

Census Division	Composite ID	Age Group[1]	Number of Individual Specimens	Number of MSAs	Percent Male	Percent Caucasian	Proportionate Tissue Amt.[2] (g)
West South Central	ACS8600494	1	10	1	50.0	70.0	2.00
	ACS8600500	2	9	1	55.6	77.8	2.22
	ACS8600519	3	8	1	50.0	75.0	2.50
East North Central	ACS8600029	1	19	3	52.6	68.4	1.05
	ACS8600038	2	17	3	100.0	100.0	1.18
	ACS8600047	2	18	3	38.9	83.3	1.11
	ACS8600056	2	20	3	0.0	80.0	1.00
	ACS8600065	3	16	3	100.0	100.0	1.25
	ACS8600074	3	11	3	36.4	0.0	1.82
	ACS8600083	3	24	4	100.0	100.0	0.83
	ACS8600092	3	19	2	42.1	0.0	1.05
	ACS8600109	3	14	3	0.0	100.0	1.43
	ACS8600118	3	16	3	0.6	100.0	1.25
	ACS8600127	3	20	1	0.0	100.0	1.00
West North Central	ACS8600449	1	12	2	58.3	91.7	1.67
	ACS8600458	2	9	2	100.0	77.8	2.22
	ACS8600467	2	11	2	0.0	90.9	1.82
	ACS8600476	3	10	2	100.0	100.0	2.00
	ACS8600485	3	12	2	0.0	100.0	1.67

Table 3-2. (cont.)

Census Division	Composite ID	Age Group[1]	Number of Individual Specimens	Number of MSAs	Percent Male	Percent Caucasian	Proportionate Tissue Amt.[2] (g)
Mountain	ACS8600225	1	3	1	0.0	100.0	6.67
	ACS8600234	2	8	2	25.0	87.5	2.50
	ACS8600243	3	12	2	100.0	83.3	1.67
	ACS8600252	3	11	2	0.0	90.9	1.82
Pacific	ACS8600305	1	9	2	77.8	66.7	2.22
	ACS8600314	2	6	2	33.3	83.3	3.33
	ACS8600323	3	16	3	100.0	93.8	1.25
	ACS8600332	3	12	2	0.0	100.0	1.67
	ACS8600341	3	7	2	0.0	0.0	2.86
	ACS8600350	3	11	2	0.0	100.0	1.82

(1) Age groups: 1 = 0-14 years; 2 = 15-44 years; 3 = 45+ years.

(2) Proportionate Tissue Amount = the approximate amount of tissue (g) contributed by each individual specimen, where the total composite weight is assumed to be 20 g.

4.0 CHEMISTRY

The 50 composite samples in the FY86 NHATS were prepared by MRI in the analysis laboratory for determination of semivolatile compounds using high-resolution gas chromatography/ mass spectrometry (HRGC/MS). The performance of the analysis effort was demonstrated through recoveries of surrogate compounds and internal quantitation standards (IQS), as well as through analysis on 20 QC samples (method blanks, control tissue samples, and spiked control tissue samples).

Section 4.1 discusses the various steps in the analytical procedure, including how results are quantified. Section 4.2 presents the QA/QC methods that were implemented. The presentation of the results for analysis of QC samples is primarily relegated to Chapter 5. Section 4.3 presents data quality objectives established for the laboratory analytical method and the extent to which these objectives were met.

4.1. ANALYTICAL PROCEDURES

The analytical procedures performed in the FY86 NHATS included the extraction and cleanup of the composite tissue samples using Gel Permeation Chromatography (GPC) and Florisil column fractionation, the analysis by HRGC/MS, and the quantitation of results. A flow diagram of these activities is found in Figure 4-1. Each of these procedures is described in detail below.

4.1.1. Sample Preparation

The preparation of the composited adipose tissue specimens for determination of semivolatiles required a multistep procedure. The stages of this procedure include quantitative extraction and cleanup through several chromatographic columns. These stages are described below.

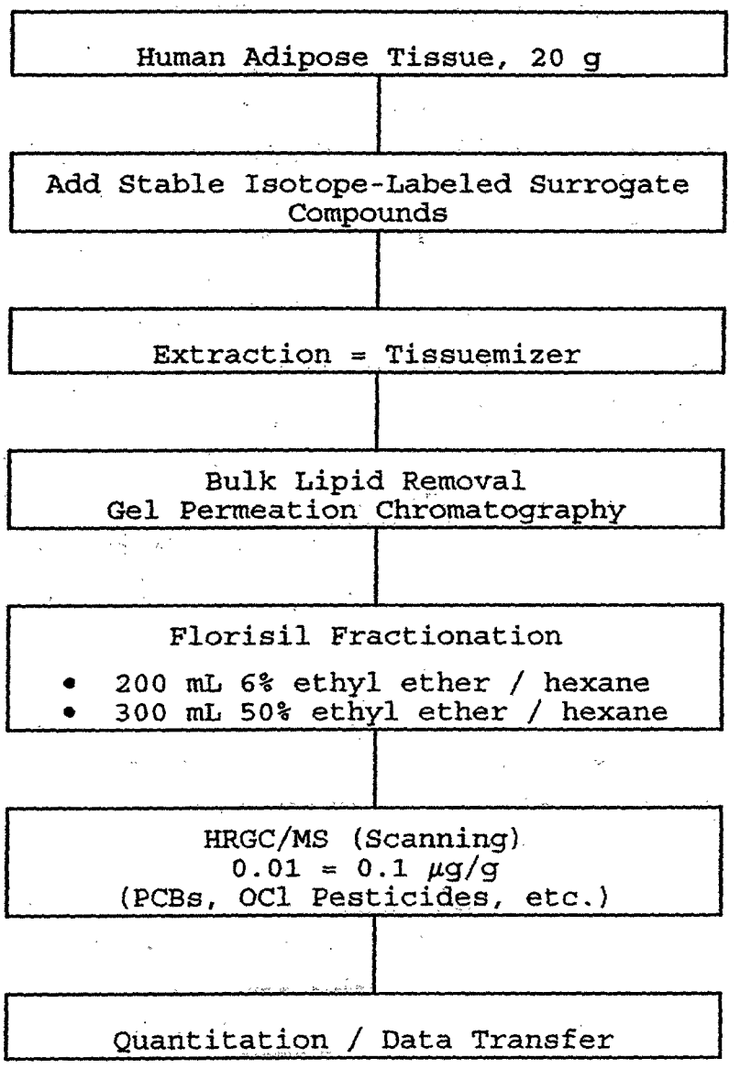

Figure 4-1. Flow Scheme for Analysis of Semivolatile Compounds in the FY86 NHATS

4.1.1.1. Extraction. After the compositing stage (Chapter 3), the adipose composites were stored at -10°C in 50-mL culture tubes sealed with aluminum foil. To begin the sample extraction procedure, the samples were allowed to come to room temperature and then fortified with 200 µL of the surrogate spiking solution. Spiked control QC samples were fortified with 50 µL and 200 µL of the native compound spiking solution for the low- and high-dose samples, respectively. Ten milliliters of methylene chloride was added and the sample homogenized for 1 min with a Tekmar Tissuemizer. The mixture was allowed to separate, and the methylene chloride was decanted through a funnel of 5 to 10 g of sodium sulfate into a 200-mL volumetric flask. The funnel was rinsed with 10 mL of methylene chloride into the volumetric flask. The homogenization was repeated two times with fresh 10-mL portions of methylene chloride. The culture tube was rinsed with additional methylene chloride and the remaining contents of the tube transferred to the funnel. Finally, the funnel was rinsed with additional methylene chloride until the volumetric flask was brought up to volume (200 mL).

4.1.1.2. Lipid Determination. At this point the flask was stoppered, inverted several times to mix the extract, and 1 mL was removed with a disposable pipet and placed into a preweighed (measured to 0.0001 g) 1-dram glass vial. The methylene chloride in the vial was reduced under nitrogen until an oily residue remained. The weight of the lipid was obtained by difference, and the percent lipid for the composite was calculated and recorded.

4.1.1.3. Extract Concentration. The remaining portion of the extract (99 mL) was quantitatively transferred, with a 30- to 40-mL rinse, to a 500-mL Kuderna-Danish evaporator equipped with a 20-mL receiver. One or two clean boiling chips and a three-ball Snyder column were added to the flask. The Snyder column was prewet with 1 mL of methylene chloride and the volume reduced to

15 to 25 mL over a steam bath. The apparatus was removed from the steam bath and allowed to cool. The flask and joint were rinsed with 5 mL of methylene chloride into the receiver. The extract was then quantitatively transferred to a 40-mL sample vial with a TFE-lined screw cap, adjusting the volume to approximately 40 mL with methylene chloride.

4.1.2. Cleanup Procedure

4.1.2.1. Gel Permeation Chromatography. GPC columns were packed with 60 g of Bio-Beads SX-3 that had been allowed to swell overnight in methylene chloride:cyclohexane (50:50). The beads were allowed to settle to form a uniform packing. Solvent, methylene chloride:cyclohexane (50:50), was pumped through the column at a flow rate of 5 mL/min. After air had been displaced from the column, the pressure was adjusted to 5 to 15 psi.

The GPC column was then calibrated using a solution of approximately 1 mg/mL butyl benzyl phthalate, 1 mg/mL 4-nitrophenol, and 390 mg/mL extracted bulk human lipid in methylene chloride. The calibration resulted in a GPC program that provided 135 mL (27 minutes) of eluent with lipid directed to a discard fraction, followed by a 225 mL (45 minute) collection period. This was the chromatographic pattern established from the elution of the butyl benzyl phthalate through the elution of 4-nitrophenol. An additional wash time of 50 mL (10 minutes) was included to prevent sample carryover.

Prior to loading the GPC, the sample collection tubes and injector port were rinsed with acetone, methylene chloride, toluene, and hexane. Syringes, beakers, and filters were washed with soap and water, rinsed with water, deionized water, acetone, methylene chloride, toluene, and hexane. All extracts were drawn through a Millipore stainless steel Swinney filter with a 0.5-μm type FH membrane. Sample loops were rinsed with 5 mL of methylene chloride:cyclohexane (50:50) and loaded with 2 mL of the sample extracted followed by 3 mL of solvent. One loop between

each composite was used as an eluent blank. The cleaned extracts were collected in clean 4-L amber solvent bottles.

4.1.2.2. GPC Eluent Concentration. The cleaned extracts from the combined GPC effluent was concentrated, using 500- or 1000-mL Kuderna-Danish (K-D) evaporators, to approximately 10 mL. The Snyder column was prewet with methylene chloride and a new boiling chip added with addition of eluent. When all the eluent was concentrated to 5 to 10 mL, the apparatus was allowed to cool. If the extract remained highly colored or viscous, the sample was quantitatively loaded onto the GPC and reprocessed in three to four loops. Then the extract was reconcentrated and transferred to Florisil as follows. If the sample extract appeared clean, 50 mL of hexane was added. The Snyder column was replaced and prewet with 1 mL of hexane. The volume was reduced to 10 mL and the flask and lower joint rinsed with 1 to 2 mL of hexane into the concentrator tube. The extract was then concentrated to approximately 1 mL under a gentle stream of purified nitrogen.

4.1.2.3. Florisil Column Cleanup. A 25- x 300-mm chromatographic column with solvent reservoir and TFE stopcock was prepared by packing the bottom with a small wad of silanized glass wool and rinsing with 20 mL of hexane. A 100-mL aliquot of hexane was added to the column. The precleaned Florisil was allowed to cool in a desiccator, and 12.5 grams were transferred to the column. When the Florisil had settled, sufficient anhydrous sodium sulfate was added to achieve a one-half inch layer on top of the Florisil. The hexane was drained just to the top of the anhydrous sodium sulfate layer. The extract was transferred to the top of the column. The extract receptacle was rinsed with three successive 2- to 3-mL aliquots of hexane, adding the rinses to the column.

A 500-mL K-D flask and receiver were placed under the column, and the sample was drained onto the column until the

anhydrous sodium sulfate was nearly exposed. The column was eluted with 200 mL of 6% ethyl ether in hexane (v/v) (Fraction 1) at a rate of about 5 mL/min. The K-D flask and receiver were replaced with another K-D flask and receiver. The column was eluted with 300 mL of 50% ethyl ether in hexane (v/v) (Fraction 2).

The fractions were concentrated to approximately 10 mL using hexane to prewet the Snyder column. The flask and lower joint were rinsed with 1 to 2 mL of hexane. The receiver was then placed under a gentle stream of purified nitrogen and the volume reduced to less than 1 mL.

If either fraction remained highly colored, viscous, or turbid, it was rediluted in methylene chloride and loaded again on the GPC. If the sample appeared clean, the sample was transferred to a clean precalibrated reactivial. The receiver was rinsed with three 1-mL aliquots of hexane, adding the rinse to the reactivial. The volume was reduced to less than 0.5 mL, the vials sealed, and the samples refrigerated.

All 6% fractions were reduced to 200 μL under a gentle stream of purified nitrogen. The 6% fractions were fortified with 200 μl of an internal quantitation standard (IQS) solution and the volume returned to 200 μL under a gentle stream of purified nitrogen. The IQS solution included naphthalene-d_8, anthracene-d_{10}, and benzo[a]anthracene-d_{12}. An aliquot of each sample was transferred to an autosampler vial and submitted for HRGC/MS analysis.

The 50% fractions were further reduced under a gentle stream of purified nitrogen. The 50% fractions were further reduced under a gentle stream of purified nitrogen. A white precipitate formed in some samples. The volume was reduced to 200, 400, or 600 μL, depending upon the volume of precipitate. An aliquot of the IQS solution equal to the sample volume was added, and then the samples were concentrated to the same volume

they had prior to addition of the IQS solution. An aliquot of each sample was submitted for HRGC/MS analysis.

4.1.3. Analysis Procedures

The quality assurance program plan for the FY84 and FY86 NHATS analysis of composite samples (Stanley et. al., 1986) describes in detail the analytical methodology for the HRGC/MS analysis of semivolatiles in the FY86 NHATS. Additional information related to the method can also be found in USEPA (1986). Specific differences in the methods between these three surveys are discussed in Chapter 8. Sections of these reports relevant to the FY86 approach are included below.

At the beginning of each day that analyses were performed, the analyst verified that the instrument was properly calibrated through analysis of decafluorotripheylphosphine (DFTTP, see Section 4.2.1). The analyst documented whether the DFTTP criteria were satisfied.

Prior to beginning analysis, a hexane blank was injected to document system cleanliness. If any evidence of system contamination was found, then another hexane blank was analyzed.

Two microliters (determined to nearest 0.1 μL) of the spiked sample extract were injected into the HRGC/MS system using a splitless injection technique. The syringe was carefully cleaned between injections by the following procedure to prevent carryover of contaminants:

- Rinse the syringe 10 times with hexane;
- Fill the syringe with toluene and sonicate syringe and plunger in toluene for 5 min and repeat at least twice;
- Rinse the syringe 10 times with hexane.

After applying this procedure, the syringe was ready for use.

Instrument performance was monitored by examining and recording the peak areas for the three IQS. If these areas

decreased to less than 50% of the calibration standard, then sample analyses were stopped until the problem was found and corrected.

The recommended HRGC/MS operating conditions for the semivolatile organic compounds are listed in Table 4-1:

Table 4-1. Recommended HRGC/MS Operating Conditions

Column temperature column	60°C (2 min) then 10°C/min to 310°C (10 min)
Injector temperature	250°C
HRGC/MS interface	300°C
Carrier gas	Helium at 30 cm/sec
Injector technique	2 μL, splitless with a 45-second delay, a split flow of 30 mL/min, and a septum purge of 5 mL/min
Electron energy	70 eV (nominal)
Mass range	40-550 amu

4.1.4. Quantitation/Data Reduction

In this subsection, the procedures for the data reduction are outlined for the analysis of data from the HRGC/MS method for semivolatile compounds. The data for each sample were interpreted with computer-assisted quantitation routines. A mass spectral library and quantitation list of the target analytes based on relative retention times and the primary characteristic ion were used to search each data file.

4.1.4.1. Qualitative Identification. The quantitation routine identified positive responses based on the primary or secondary characteristic ion for each of the analytes. Table 4-2 provides a list of these analytes (native compounds, surrogates, and IQS), along with the primary and secondary quantitation ions used for compound characterization.

Table 4-2. Characteristic Masses and Intensities for the Qualitative Identification of the Semivolatile Target Analytes, Chromatographic Conditions, and Estimated Limit of Detection

Compound	Characteristic Masses (m/z)			Relative Retention Time[1]	Est. Limit of Detection (µg/g)[2]	Internal Quantitation Standard
	Primary	Secondary	Secondary			
Organochlorine Pesticides						
p-p'-DDT	235 (100)[3]	237 (72)	165 (48)	1.33-1.39	0.010	Anthracene-d_{10}
o,p'-DDT	235 (100)	237 (66)	165 (59)	1.29-1.35	0.010	Anthracene-d_{10}
p,p'-DDE	246 (100)	248 (58)	176 (41)	1.23-1.29	0.010	Anthracene-d_{10}
o,p'-DDE	246 (100)	248 (64)	176 (38)	1.19-1.25	0.010	Anthracene-d_{10}
p,p'-DDD	235 (100)	237 (66)	165 (58)	1.28-1.34	0.010	Anthracene-d_{10}
o,p'-DDD	235 (100)	237 (66)	165 (58)	1.24-1.30	0.010	Anthracene-d_{10}
α-BHC	183 (100)	181 (96)	219 (68)	0.90-0.96	0.010	Anthracene-d_{10}
β-BHC	183 (100)	181 (96)	219 (81)	0.95-1.00	0.010	Anthracene-d_{10}
γ-BHC (lindane)	183 (100)	181 (96)	219 (66)	0.95-1.01	0.010	Anthracene-d_{10}
δ-BHC	183 (100)	181 (96)	219 (81)	0.99-1.05	0.010	Anthracene-d_{10}
Aldrin	263 (100)	265 (67)	261 (63)	1.09-1.15	0.010	Anthracene-d_{10}
Dieldrin	263 (100)	265 (58)	279 (58)	1.23-1.29	0.050	Anthracene-d_{10}
Endrin	263 (100)	265 (66)	279 (38)	1.26-1.44	0.050	Anthracene-d_{10}
Heptachlor	100 (100)	272 (35)	274 (30)	1.08-1.14	0.010	Anthracene-d_{10}
Heptachlor epoxide	353 (100)	355 (83)	351 (56)	1.16-1.21	0.010	Anthracene-d_{10}
Oxychlordane	115 (100)	185 (35)	187 (30)	--	0.010	Anthracene-d_{10}
Mirex	272 (100)	274 (82)	270 (51)	1.46-1.52	0.010	Benzo[a]anthracene-d_{12}
trans-Nonachlor	409 (100)	407 (91)	411 (65)	1.21-1.27	0.010	Anthracene-d_{10}

Table 4-2. (cont.)

Compound	Characteristic Masses (m/z)			Relative Retention Time[1]	Est. Limit of Detection (µg/g)[2]	Internal Quantitation Standard
	Primary	Secondary	Secondary			
γ-Chlordane	373 (100)	375 (99)	377 (50)	1.19-1.24	0.010	Anthracene-d_{10}
Polychlorinated Biphenyls (PCBs)						
Monochloro- (3-isomers)	188 (100)	190 (33)	--	0.63-0.86	0.010	Anthracene-d_{10}
Dichloro- (12-isomers)	222 (100)	224 (66)	226 (11)	0.81-0.95	0.010	Anthracene-d_{10}
Trichloro- (24-isomers)	256 (100)	258 (99)	260 (33)	0.81-1.10	0.010	Anthracene-d_{10}
Tetrachloro- (42-isomers)	292 (100)	290 (76)	294 (49)	0.90.1.30	0.010	Anthracene-d_{10}
Pentachloro- (46-isomers)	326 (100)	328 (66)	324 (61)	1.05-1.40	0.020	Anthracene-d_{10}
Hexachloro- (42-isomers)	360 (100)	362 (82)	358 (51)	1.25-1.49	0.020	Benzo[a]anthracene-d_{12}
Heptachloro- (24-isomers)	394 (100)	396 (98)	392 (44)	1.30-1.61	0.020	Benzo[a]anthracene-d_{12}
Octachloro- (12-isomers)	430 (100)	428 (87)	432 (66)	1.40-1.55	0.020	Benzo[a]anthracene-d_{12}
Nonachloro- (3-isomers)	464 (100)	462 (76)	466 (76)	1.49-1.61	0.020	Benzo[a]anthracene-d_{12}
Decachloro- (1-isomer)	498 (100)	500 (87)	496 (68)	1.61-1.67	0.050	Benzo[a]anthracene-d_{12}
Chlorobenzenes						
Trichloro- (3-isomers)	180 (100)	182 (98)	184 (32)	0.36-0.60	0.010	Naphthalene-d_8
Tetrachloro- (3-isomers)	216 (100)	214 (77)	218 (49)	0.55-0.80	0.010	Naphthalene-d_8
Pentachlor-	250 (100)	252 (65)	248 (61)	0.76-0.82	0.010	Anthracene-d_{10}
Hexachloro-	284 (100)	286 (82)	282 (51)	0.91-1.00	0.010	Anthracene-d_{10}

Table 4-2. (cont.)

Compound	Characteristic Masses (m/z)			Relative Retention Time[1]	Est. Limit of Detection (µg/g)[2]	Internal Quantitation Standard
	Primary	Secondary	Secondary			
Phthalate Esters						
Dimethyl phthalate	163 (100)	194 (11)	164 (10)	0.70-0.76	0.010	Anthracene-d_{10}
Diethyl phthalate	149 (100)	177 (31)	150 (12)	0.82-0.87	0.010	Anthracene-d_{10}
Di-n-butyl phthalate	149 (100)	150 (19)	104 (9)	1.08-1.14	0.010	Anthracene-d_{10}
Butyl benzyl phthalate	149 (100)	167 (38)	279 (-)	1.33-1.38	0.010	Benzo[a]anthracene-d_{12}
Di-n-octyl phthalate	149 (100)	167 (41)	--	1.43-1.48	0.010	Benzo[a]anthracene-d_{12}
Bis(2-ethylhexyl) phthalate	149 (100)	167 (35)	279 (11)	1.50-1.60	0.010	Benzo[a]anthracene-d_{12}
Phosphate Triesters						
Tributyl phosphate	99 (100)	155 (27)	211 (16)	0.86-0.92	0.050	Anthracene-d_{10}
tris(2-Chloroethyl) phosphate	143 (100)	249 (95)	251 (60)	0.95-1.00	0.040	Anthracene-d_{10}
tris(Dichloropropyl) phosphate	99 (100)	191 (65)	209 (45)	1.32-1.38	0.050	Benzo[a]anthracene-d_{12}
Tributoxyethyl phosphate	101 (100)	325 (99)	170 (32)	1.36-1.46	0.020	Benzo[a]anthracene-d_{12}
Tritolyl phosphate	91 (100)	165 (80)	368 (77)	1.46-1.57	0.020	Benzo[a]anthracene-d_{12}
Triphenyl phosphate	326 (100)	325 (65)	170 (24)	1.31-1.37	0.020	Benzo[a]anthracene-d_{12}
Polynuclear Aromatic Hydrocarbons (PAH)						
Naphthalene	129 (100)	129 (12)	127 (11)	0.46-0.52	0.010	Naphthalene-d_8
Acenaphthylene	152 (100)	151 (17)	153 (16)	0.70-0.76	0.010	Anthracene-d_{10}
Acenaphthene	154 (100)	153 (86)	152 (43)	0.73-0.79	0.010	Anthracene-d_{10}
Fluorene	166 (100)	165 (83)	167 (14)	0.81-0.87	0.010	Anthracene-d_{10}

Table 4-2. (cont.)

Compound	Characteristic Masses (m/z)			Relative Retention Time[1]	Est. Limit of Detection (µg/g)[2]	Internal Quantitation Standard
	Primary	Secondary	Secondary			
Phenanthrene	178 (100)	179 (16)	176 (18)	0.97-1.02	0.010	Anthracene-d_{10}
Fluoranthene	202 (100)	101 (23)	100 (14)	1.16-1.22	0.010	Anthracene-d_{10}
Pyrene	202 (100)	101 (26)	100 (17)	1.20-1.25	0.010	Anthracene-d_{10}
Chrysene	228 (100)	226 (22)	229 (22)	1.40-1.46	0.010	Benzo[a]anthracene-d_{12}
Surrogate Compounds						
1,2,4-Trichlorobenzene-d_3	183 (100)	185 (98)	187 (32)	0.36-0.60	0.010	--
Chrysene-d_{12}	240 (100)	238 (22)	241 (22)	1.40-1.46	0.010	Benzo[a]anthracene-d_{12}
$^{13}C_6$-1,2,4,5-tetrachlorobenzene	222 (100)	220 (77)	224 (49)	0.55-0.80	0.010	Naphthalene-d_8
$^{13}C_6$-hexachlorobenzene	292 (100)	292 (82)	288 (51)	0.91-1.00	0.010	Naphthalene-d_8
$^{13}C_6$-4-chlorobiphenyl	194 (100)	196 (33)	--	0.63-0.86	0.010	Anthracene-d_{10}
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	304 (100)	302 (76)	306 (49)	0.90-1.30	0.010	Anthracene-d_{10}
$^{13}C_{12}$-2,2',3,3',4,4'5,5'-octachlorobiphenyl	442 (100)	440 (87)	444 (66)	1.40-1.55	0.020	Benzo[a]anthracene-d_{12}
$^{13}C_{12}$-decachlorobiphenyl	510 (100)	512 (87)	508 (68)	1.61-1.67	0.050	Benzo[a]anthracene-d_{12}
Diethyl phthalate-3,4,5,6-d_4	153 (100)	181 (31)	154 (12)	0.82-0.87	0.010	Anthracene-d_{10}
Di-n-butyl phthalate-2,4,5,6-d_4	153 (100)	154 (19)	108 (13)	1.08-1.14	0.010	Anthracene-d_{10}
Butyl benzyl phthalate-3,4,5,6-d_4	153 (100)	171 (38)	283 (-)	1.33-1.38	0.010	Benzo[a]anthracene-d_{12}

Table 4-2. (cont.)

Compound	Characteristic Masses (m/z)			Relative Retention Time[1]	Est. Limit of Detection (µg/g)[2]	Internal Quantitation Standard
	Primary	Secondary	Secondary			
Internal Standards						
Naphthalene-d_8	136 (100)	137 (12)	135 (11)	0.46-0.52	0.010	Anthracene-d_{10}
Anthracene-d_{10}	188 (100)	189 (16)	186 (17)	1.00	0.010	--
Benzo[a]anthracene-d_{12}	240 (100)	238 (22)	241 (22)	1.40-1.67	0.010	--

(1) Relative retention times (RRT) calculated versus the internal standard anthracene-d_{10} with chromatographic conditions as specified in Section 12.1. For napthalene-d_{10} and benzo[a]anthracene-d_{12} relative to anthracene-d_{10} are estimated to be within the range of 0.36-0.60 and 1.40-1.65, respectively.

(2) Estimated detection level for 20 g sample assuming 100% recovery of analyte. The estimate detection level for the chlorobenzenes and PCBs reflect the sensitivity for a single isomer.

(3) Values in parentheses represent the relative abundances of the characteristic masses.

The following criteria based on Table 4-2 must have been met in order to make a qualitative identification:

- The characteristic masses of each parameter of interest must maximize in the same scan or within one scan of each other.
- The retention time must fall within ±10 seconds of the retention time of the authentic compound.
- The relative peak heights of the three characteristic masses in the EICPs must fall within ±30% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.
- The response for each of the characteristic ions must be at least 2.5 times the background signal-to-noise ratio.

4.1.4.2. Quantitation. Data were quantitated on the internal standard method. IQS were paired with each analyte for quantitation purposes; these pairings are displayed in Table 4-2. Relative response factors (RRFs) for native "quantitative" semivolatile compounds were calculated from the data obtained during the analysis of calibration solutions using the following formula:

$$RRF = \frac{A_{STD} \cdot C_{IS}}{A_{IS} \cdot C_{STD}} \qquad (4\text{-}1)$$

where A_{STD} = The area of the primary quantitation ion for the analyte in question,
A_{IS} = The area of the primary quantitation ion for the labeled IQS paired with the given analyte,
C_{STD} = Concentration (ng/μL) of the analyte,
and C_{IS} = Concentration (ng/μL) of the IQS.

Once the RRF values were obtained, the lipid-adjusted concentration of a semivolatile analyte within an adipose tissue sample (C_{sample}) was calculated as follows:

$$C_{sample}(ng/g) = \frac{A_{sample} \cdot Q_{IS} \cdot 100\%}{A_{IS} \cdot RRF \cdot W_{AT} \cdot LC} \quad (4\text{-}2)$$

where RRF was determined from the calibration,

A_{sample} = The area of the primary quantitation ion for the analyte in question within the sample,

A_{IS} = The area of the primary quantitation ion for the labeled IQS paired with the analyte,

Q_{IS} = The amount (total ng) of the labeled IQS added to the sample prior to extraction,

W_{AT} = Weight (g) of the original adipose tissue sample,

and LC = Percent extractable lipid from the sample.

4.1.4.3. Recovery of Surrogate Standards. Recoveries of the labelled surrogate standards measured in the final extract were calculated using the following formula:

$$\%\ Recovery = \frac{A_{SS} \cdot Q_{IS}}{A_{IS} \cdot Q_{SS} \cdot RRF_{SS}} \cdot 100\% \quad (4\text{-}3)$$

where A_{IS} and Q_{IS} are defined above,

A_{SS} = Area of the primary quantitation ion determined for the surrogate standard,

Q_{SS} = Amount (ng) of the surrogate standard added to the sample prior to extraction,

and RRF_{SS} = RRF for the surrogate standard relative to its IQS, as determined from the initial calibration.

4.1.4.4. Data Qualifiers. Quantitative data were classified to indicate the intensity of the signal response. For quantitative compounds, the qualifiers were defined as follows:

- Not Detected (ND): S/N ratio less than 2.5.
- Trace (TR): S/N ratio at 2.5 or above, but less than 10.
- Positive Quantifiable (PQ): S/N ratio at 10 or above.

The semivolatile compounds described as "qualitative analytes" in the FY86 NHATS were not quantitated beyond a one-significant-

figure estimate. A "positive detect" (PD) was reported for analytes that met the qualitative criteria.

4.1.4.5. Estimating the Method Limit of Detection. A method limit of detection (LOD) was estimated for a given sample in the following situations for a specific analyte:

- no response was noted for the analyte;
- a response was noted but the ion ratios were incorrect;
- a response was noted but was below the calibration range; or
- the reported response was quantitated as a trace value.

If no response was noted, the LOD was reported as the lower end of the established calibration range. The LOD value was reported as total ng/injection such that the LOD could be extrapolated for each individual sample.

For samples for which a response at the compound's retention time was noted but the qualitative criteria for ion ratios were outside an acceptable range, the estimated LOD was calculated as the response of the interference, and the concentration value was regarded as not detected (ND).

If a response was noted at the correct retention time and met the qualitative criteria of ion ratio agreement for identification, but the calculated response was below the calibration curve, then the value was identified as not detected.

If a response was qualified as a trace value, then the analyst also provided an estimated LOD. This was accomplished by using the observed signal-to-noise ratio on either side of the response or the lower calibration limit, whichever was higher.

4.2. QA/QC FOR CHEMICAL ANALYSIS

4.2.1. Demonstrating Achievement of Instrument Performance Requirements

Achievement of the instrument performance requirements were demonstrated in the following stages:

(1) HRGC Column Performance A 30-m HRGC column, DB-5, film thickness = 0.2 μm, was used for analysis of all samples and standards for the 6% fraction extracts, and a 30-m DB-1301, film thickness = 0.2 μm, was used for all 50% fraction extracts. The column performance was initially demonstrated using a Grob hydrocarbon mixture. The retention times should be within ±30% of the values supplied by the manufacturer with the column when chromatographed under similar conditions. If during the course of the analysis it became necessary to install a new column, this column was verified in a similar manner.

(2) Tuning and Mass Calibration. The mass spectrometer was tuned at least daily to yield optimum sensitivity using decafluorotripheylphosphine (DFTTP). The criteria that must be met are listed in Table 4-3. Corrective actions were implemented whenever the resolving power did not meet the requirement. Examples of these corrective actions are recalibrating the mass spectrometer, changing the GC column, or maintenance of the instrument. Corrective actions were determined by consultation between the analyst, the work assignment leader(s), and the mass spectrometry facility staff.

(3) RRF Check and Instrument Sensitivity Check. As part of the initial and routine instrument performance checks, a single calibration standard was analyzed and RRF values of the respective analytes were compared to specific internal standards. The initial and routine calibration criteria require that the

Table 4-3. DFTTP Key Masses and Abundance Criteria[1]

Mass	Intensity Required
51	8%-82% of mass 198
68	<2% of mass 69
69	11%-91% of mass 198
70	<2% of mass 69
127	32%-59% of mass 198
198	base peak, 100% abundance
199	4%-9% of mass 198
275	11%-30% of mass 198
441	44%-110% of mass 443
442	30%-86% of mass 198
443	14%-24% of mass 442

[1] EPA Method 1625 Revision B: Semivolatile Organic Compounds by Isotope Dilution GC/MS, January 1985.

precision of the RRF measurements are ±30% for the target analytes.

Sensitivity of the MS was documented through the responses noted for the first calibration standard of each analysis day. The method requires that a low level standard be analyzed to document sufficient instrumental response to support instrumental detection limits.

Routine checks on the instrumental sensitivity were achieved by monitoring the response for the IQS from injection to injection and documenting the responses in the MS log book. If the response for the IQS was noted to drop by greater than 50% of the response noted in the previous calibration standard, the analyst verified instrumental performance through the analysis of an additional calibration standard.

The qualitative analytes in the FY86 NHATS were identified by relative retention times and characteristic mass peaks. These met the same qualitative identification factors as the quantitative targets but were not quantitated beyond a one-significant-figure estimate. The RRFs for the compounds were not a required factor in the initial calibration and daily performance checks. A "positive detect" (PD) was reported for analytes that met the qualitative criteria in Section 4.1.4.

4.2.2. Calibration for Quantitative Semivolatile Analysis

4.2.2.1. Initial Calibration. Initial calibration was required before any samples were analyzed, or when any routine calibration did not meet the required criteria for the consistency of RRFs (±30% for quantitative targets and internal standards). An initial calibration was conducted by performing the following steps:

(1) Tuning and calibrating the instrument with PFK and DFTTP.

Table 4-4. Calibration Solutions for the 6% Florisil Fraction

Compound	Approximate Concentration (ng/μL) in Calibration Solutions				
	CS1	CS2	CS3	CS4	CS5
Lindane (γ-BHC)	100	50	10	5	1
Mirex	100	50	10	5	1
Chlordane	100	50	10	5	1
Oxychlordane	100	50	10	5	1
Aldrin	100	50	10	5	1
α-BHC	100	50	10	5	1
Δ-BHC	100	50	10	5	1
β-BHC	100	50	10	5	1
Heptachlor epoxide	100	50	10	5	1
Heptachlor	100	50	10	5	1
p,p'-DDT	100	50	10	5	1
o,p'-DDT	100	50	10	5	1
p,p'-DDE	100	50	10	5	1
o,p'-DDE	100	50	10	5	1
o,p'-DDD	100	50	10	5	1
p,p'-DDD					
t-Nonachlor	100	50	10	5	1
1,3-Dichlorobenzene	100	50	10	5	1
1,4-Dichlorobenzene	100	50	10	5	1
1,2-Dichlorobenzene	100	50	10	5	1
1,2,4-Trichlorobenzene	100	50	10	5	1
1,2,3-Trichlorobenzene	100	50	10	5	1
1,3,5-Trichlorobenzene	100	50	10	5	1
1,2,3,4-Tetrachlorobenzene	100	50	10	5	1
1,2,3,5-Tetrachlorobenzene	100	50	10	5	1
1,2,4,5-Tetrachlorobenzene	100	50	10	5	1
Pentachlorobenzene	100	50	10	5	1
Hexachlorobenzene	100	50	10	5	1
Naphthalene	100	50	10	5	1
Phenanthrene	100	50	10	5	1

Table 4-4. (cont.)

Compound	Approximate Concentration (ng/μL) in Calibration Solutions				
	CS1	CS2	CS3	CS4	CS5
Fluoranthene	100	50	10	5	1
Chrysene	100	50	10	5	1
Benzo[a]pyrene	100	50	10	5	1
Acenaphthylene	100	50	10	5	1
Acenaphthene	100	50	10	5	1
Fluorene	100	50	10	5	1
Pyrene	100	50	10	5	1
Biphenyl	100	50	10	5	1
1,2-Dibromo-3-chloropropane	100	50	10	5	1
[illegible] (HCBD)	10[illegible]	[illegible]	10	5	[illegible]
He[illegible]lorocy[illegible]	100	[illegible]	10	[illegible]	1
Octachlorostyrene	[illegible]	50	10	5	1
Tetrabromobiphenyl	100	50	10	5	1
o-Cymene	100	50	10	5	1
m-Cymene	100	50	10	5	1
[illegible]	100	50	10	5	[illegible]
D-Limonene	100	50	10	5	1
D,L-Isoborneol	100	50	10	5	1
1-Indanone	100	50	10	5	1
2-Inadanone	100	50	10	5	1
Butylated hydroxytoluene	100	50	10	5	1
Coumarin	100	50	10	5	1
Octamethylcyclotetrasiloxane	100	50	10	5	1

(2) Analyzing the five concentration calibration solutions for the 6% fracton eluates listed in Table 4-4. The low concentration solution, CS5, was used to demonstrate the lower limit of detection provided by the available instrument.

(3) Computing the RRFs for each analyte in the concentration calibration solution using the criteria for positive identification of semivolatile analytes and the computational methods given in Section 4.1.4.

(4) Computing the means and their respective relative standard deviations (RSD, expressed as a percentage) for the RRFs for each analyte in the standard. The RSD was calculated as the standard deviation to all measurements of a particular RRF value divided by the average RRF value and multiplied by 100%. These samples were identified in the individual batch reports.

(5) Repeating the above process for the 50% Florisil fraction eluates (Table 4-5) and PCB calibration solution (Table 4-6).

The above fractionation was based on the previous broad scan analysis of adipose tissue. In the case of quantitative analytes not previously determined, comparisons to similar compounds have been made for the purpose of determining in which Florisil fraction the analyte was most likely to appear.

To declare an acceptable initial calibration, the RSD for the response factors for the analysis of analytes across the calibration range must have been less than ±30%. If this criterion held, then the RRF was assumed to be nonvariant and the average RRF could be used for calculating a RSD value. Alternatively, the results were used to plot a calibration curve of response ratios, A_3/A_{is} versus RRF.

An acceptable initial calibration also required the traces for all ions used for quantitation to present a signal-to-noise (S/N) ratio of at least 2.5. This included analytes and isotopically labeled standards. Isotopic ratios must have been within ±30% of the theoretical values.

Table 4-5. Calibration Solutions for the 50% Florisil Fraction

Compound	Approximate Concentration (ng/μL) in Calibration Solutions				
	CS1	CS2	CS3	CS4	CS5
Dimethyl phthalate	100	50	10	5	1
Dibutyl phthalate	100	50	10	5	1
Butylbenzyl phthalate	100	50	10	5	1
Di-n-octyl phthalate	100	50	10	5	1
Diethyl phthalate	100	50	10	5	1
Di-n-butyl phthalate	100	50	10	5	1
Tributyl phthalate	100	50	10	5	1
Diethylhexylphthalate (DEHP)	100	50	10	5	1
Tributylphosphate	500	250	50	25	5
Triphenylphosphate	200	100	20	10	2
Tris(2-chloroethyl)phosphate	500	250	50	25	5
Tributoxyethylphosphate	200	100	20	10	2
Tritolylphosphate	200	100	20	10	2
Tris(dichloropropyl)phosphate	500	250	50	25	5
Dieldrin	500	250	50	25	5
Endrin	500	250	50	25	5
Endrin ketone	500	250	50	25	5
Tris(2,3-dibromopropyl)-phosphate	500	250	50	25	5
2-Phenylphenol	100	50	10	5	1
Trichloro-o-terphenyl	200	100	20	10	2
Tetrachloro-o-terphenyl	200	100	20	10	2
4-Chloro-o-terphenyl	200	100	20	10	2
Pentachlorodiphenyl ether	200	100	20	10	2
2-Methoxy-3-methylpyrazine	200	100	20	10	2
Ethyl hydrocinnamate	200	100	20	10	2

Table 4-6. Calibration Solutions for PCB Analysis

Compound	Approximate Concentration (ng/μL) in Calibration Solutions				
	CS1	CS2	CS3	CS4	CS5
Monochlorobiphenyl	100	50	10	5	1
Dichlorobiphenyl	100	50	10	5	1
Trichlorobiphenyl	100	50	10	5	1
Tetrachlorobiphenyl	100	50	10	5	1
Pentachlorobiphenyl	200	100	20	10	2
Hexachlorobiphenyl	200	100	20	10	2
Heptachlorobiphenyl	200	100	20	10	2
Octachlorobiphenyl	200	100	20	10	2
Nonachlorobiphenyl	200	100	20	10	2
Decachlorobiphenyl	500	250	50	25	5

4.2.2.2. Routine Calibrations. Routine calibrations were performed at the beginning of every day before actual sample analyses were performed and as the last injection of every day. Routine calibrations involved the following steps:

(1) Injecting 2 μL of the concentration calibration solutions CS3 for the 6% fraction as the initial calibration check on each analysis day and as the final check on each analysis day.

(2) Computing the RRFs for each analyte in the concentration calibration solution using the criteria for positive identification of semivolatiles given in Section 4.1.4.

To declare an acceptable routine calibration, the measured RRF for all analytes must have been within ±30% of the mean values established by initial calibration of the calibration concentraton solutions. Also, isotopic ratios must have been within ±30% of the theoretical value for each analyte and isotopically labeled standard.

4.2.3. Spiking Solution Preparation

4.2.3.1. Native Standard Spiking Solution. A native standard spiking solution was prepared in dichloromethane from the individual stock standards. This solution was used for preparing laboratory spikes of adipose tissue. For example, if the anticipated spike level is 0.10 μg/g in a 20-g sample, the target analyte should be added to the spiking solution to achieve a final concentration of 10 μg/mL. The specific PCB isomers used for preparing calibration solutions were also included in the target spiking solution. The spiking solution and proposed levels are listed in Table 4-7.

4.2.3.2. Surrogate Standard Spiking Solution. A mixed surrogate standard spike solution was prepared in dichloromethane from the individual stock standards. The surrogate standard spike

Table 4-7. Proposed QC Spiking Solutions

Compound	Approximate Spike Solution Conc (ng/μL)	Final Spike Volume (μL)[1]	
		S1	S2
p,p'-DDE	29.5	200	50
p,p'-DDT	28.4	200	50
Dieldrin	21.9	200	50
Heptachlor epoxide	14.3	200	50
t-Nonachlor	21.9	200	50
Mirex	21.7	200	50
γ-Chlordane	22.3	200	50
Hexachlorobenzene	19.5	200	50
1,2,4,5-Tetrachlorobenzene	28.8	200	50
1,4-Dichlorobenzene	124	200	50
1,2,4-Trichlorobenzene	20.7	200	50
Diethyl phthalate	23.0	200	50
Butylbenzyl phthalate	22.6	200	50
Triphenyl phosphate	19.2	200	50
Tris(dichloroethyl)phosphate	372	200	50
Benzo[a]pyrene	24.1	200	50
Phenanthrene	23.6	200	50
Chrysene	5.07	200	50
Hexachloro-1,3-butadiene	19.6	200	50
R-Limonene	23.4	200	50
2-Phenyl phenol	20.7	200	50
Coumarin	25.2	200	50
o-Cymene	28.0	200	50
2-Indanone	17.3	200	50
DL-Isoborneol	26.7	200	50
Ethyl hydrocinnamate	32.7	200	50
Octamethylcyclotetrasiloxane	21.1	200	50
Monochlorobiphenyl	25.3	200	50
Dichlorobiphenyl	27.9	200	50
Trichlorobiphenyl	24.6	200	50

Table 4-7. (cont.)

Compound	Approximate Spike Solution Conc (ng/μL)	Final Spike Volume (μL)[1]	
		S1	S2
Tetrachlorobiphenyl	56.2	200	50
Pentachlorobiphenyl	65.0	200	50
Hexachlorobiphenyl	52.6	200	50
Heptachlorobiphenyl	130	200	50
Octachlorobiphenyl	137	200	50
Nonachlorobiphenyl	154	200	50
Decachlorobiphenyl	96.1	200	50

(1) Final spike level is based on ng of analyte/g of adipose (20 g sample). The actual reported value would be based on ng of analyte/g of extractable lipid.

(2) From EPA Method 680 list except for the nonachlorbiphenyl which is not included in Method 680.

solution were prepared to deliver the surrogates at the amounts specified in Table 4-8 in a 200-μL volume. This requires that the stock solution contain the surrogates at concentrations ranging from 10 to 50 μg/mL.

4.2.3.3. Internal Standard Spiking Solution. The internal standard spiking stock solution concentrations are also listed in Table 4-8 for each of the deuterated internal standards.

4.2.3.4. Performance Audit Solutions. Included among the samples in at least two sample batches was a solution provided by the quality control coordinator containing known amounts of specific target analytes representing each major compound class to be determined. The accuracy of measurements for performance evaluation samples was in the range of 70-130%.

4.2.4. QC Samples

Samples included for QC purposes within each batch of composite samples are summarized in Table 4-9. The order of preparation and analysis with respect to the FY86 NHATS composites was specified in the sample design. This section discusses each of these QC sample types. Discussion of the findings and conclusions from QC sample analyses are presented in Section 5.3.

4.2.4.1. Method Blanks. One method blank was generated within each batch of samples. A method blank was generated by performing all steps detailed in the analytical procedure using all reagents, standards, equipment, apparatus, glassware, and solvents that were used for a sample analysis, but not adding any adipose tissue. The method blank contained the same amounts of labeled surrogate standards that were added to samples before bulk lipid cleanup.

Protocol dictated that if the levels detected in the method blank were greater than 10% of the levels seen in the

Table 4-8. Spike Levels for Surrogate and Internal Standards[1]

Analyte	Spike Levels (μg)[2]
Surrogate Compounds	
1,2,4-Trichlorobenzene-d_6	3.428
Chrysene-d_{12}	2.808
$^{13}C_6$-1,2,4,5-Tetrachlorobenzene	2.470
$^{13}C_6$-Hexachlorobenzene	1.932
$^{13}C_6$-4-Chlorobiphenyl	2.222
$^{13}C_{12}$-3,3',4,4'-Tetrachlorobiphenyl	4.016
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-Octachlorobiphenyl	6.852
$^{13}C_{12}$-Decachlorobiphenyl	12.20
Diethyl phthalate-3,4,5,6-d_4[3]	2.252
Di-n-butyl phthalate-3,4,5,6-d_4[3]	1.800
Lindane $^{13}C_6/d_6$	1.672
Heptachlor ^{13}C	2.030
Internal Standards	
Naphthalene-d_8	1.901
Anthracene-d_{10}	1.910
Benzo[a]anthracene-d_{12}	2.102

(1) Refer to EPA Method 1625, Revision B--Semivolatile Organic Compounds by Isotope Dilution GC/MS, Federal Register 1984, 49 (209), pp. 184-197.

(2) Concentration calculated for a solution of 200-μL final volume.

(3) Were not reported in most samples.

Table 4-9. Quality Control Samples Included in the FY86 NHATS Analytical Procedure

Type	Frequency	Application
Method blank	One per batch	Assess laboratory background contribution.
Spiked control adipose tissue sample	Two per batch (two different spike levels)	Evaluate method performance (accuracy and precision)
Unspiked control adipose tissue sample	One per batch	Evaluate method performance (accuracy and precision)

tissue samples, then the solvents, reagents, spiking solutions, apparatus, and glassware were checked to locate and eliminate the source of contamination before any further samples were extracted and analyzed.

4.2.4.2. Control Samples. Control samples were prepared from a bulk sample of approximately 2 kg of human adipose tissue. This material was prepared by blending the tissue with methylene chloride, drying the extract by eluting through anhydrous sodium sulfate, and removing the methylene chloride using rotoevaporation at elevated temperatures (80°C). The evaporation process was extended to ensure all traces of the extraction solvent have been removed. The resulting oily matrix (lipid) was subdivided into 20-g aliquots which were analyzed with each sample batch.

4.2.4.3. Spiked Control Samples. Spiked lipid samples were prepared by using a portion of the homogenized lipid. Sufficient spiked lipid matrix was prepared to provide a minimum of two spiked samples per sample batch: one sample spiked at a low concentration and one at a high concentration. Method performance was addressed in this study by calculating recoveries for each spiked sample as follows:

$$\text{Recovery}(\%) = \frac{\text{conc. (spiked sample)} - \text{conc. (control sample)}}{\text{Spike level}} * 100 \quad (4\text{-}4)$$

This method to calculating percent recovery leads to a test of ruggedness of the method with respect to detecting finite differences in concentration. Note that an equally-accepted approach to calculating percent recovery is given by the formula

$$\textit{Recovery}(\%) = \frac{\textit{conc. (spiked sample)}}{\textit{conc. (control sample)} + \textit{spike level}} * 100\% \quad (4\text{-}5)$$

Formula (4-5) can lead to larger percentages than formula (4-4) applied in this study. This fact should be considered when interpreting observed recovery percentages in this study.

Analytical results of the QC samples are statistically summarized in Chapter 5. This chapter also presents conclusions and issues resulting from the QC sample analysis.

4.3 OVERALL DATA QUALITY

At the outset of the analysis effort for the FY86 NHATS, specific data quality objectives were defined for the quantitative and qualitative analyses of the target semivolatile compounds. Data quality objectives were established for calibration criteria (relative response factors [RRFs]) for each analyte and internal standard, internal standard response area, and method performance based on the recoveries of labeled surrogate compounds and native compounds spiked into a spiked internal QC sample. The data generated with respect to these criteria are presented within this report. Further details were provided in the original data reports.

Table 4-10 summarizes the performance achieved versus the specific criteria and data quality objectives for the analysis of the FY86 NHATS composites.

Table 4-10. Data Quality Objectives for the FY86 NHATS, Along With Actual Performance

Criteria	Objective	Actual Performance
RRF calibration	±30% all quantitative analytes	>90% of all RRF factors within DDQs.
Labeled surrogate standards	40%-160%	>84% for all labeled surrogate spikes; 12% of the deviation due to 50% fraction surrogates.
Spiked internal QC samples	50%-150%	70% of all measurements within criteria; 22% of all deviations due to 50% fraction compounds.
Internal standard response areas	50%-150% of initial daily calibration standard	>90% of all measurements within criteria.

5.0 DATA ISSUES

The NHATS FY86 sampling effort resulted in a total of 50 composites of adipose tissue specimens for chemical analysis (see Chapter 3). In the analytic laboratory, these 50 composites were partitioned into five groups, or *batches*, of ten composites each. Each batch also included the following four laboratory QC samples:

- One method blank
- Three samples prepared from a homogeneous bulk lipid extract; two of these samples spiked at differing levels by selected native compounds.

Thus, the NHATS FY86 chemical analysis was performed on five batches each containing fourteen analytical samples, for a total of 70 analytical samples. Samples within a batch were chemically analyzed as a group under similar laboratory conditions.

Prior to chemical analysis, all non-blank analytical samples were spiked with a set of twelve surrogate compounds. These labelled compounds do not exist in the natural environment and were selected to represent the native compounds of interest. Analysis of surrogate recovery data was performed to evaluate method performance and overall recovery levels.

This chapter addresses a series of preliminary data issues which include a summary of the composite data and statistical analysis on the QC data. The information gathered from this preliminary data investigation was essential for the statistical analysis and interpretation of sample results. The objectives of the preliminary data analysis included the following:

- Identify those compounds having a sufficiently large percentage of composite samples with detected results. Results for these compounds will likely reflect more accurate estimates of average concentration levels and variability.

- Identify the extent that systematic errors in measured concentrations are present over time by considering surrogate recovery data. If necessary, adjust the measured concentrations for these errors.

- Characterize method performance through analysis of QC sample data, identifying sources of variability and the extent of batch effects in the (adjusted) measured concentrations.

Each of these efforts is documented in separate subsections which follow.

5.1 DETERMINING NATIVE COMPOUNDS TO INCLUDE IN STATISTICAL ANALYSIS

A total of 111 semivolatile compounds were considered in the FY86 NHATS. These compounds fall into several chemical classes:

- Pesticides (19 compounds)
- Chlorobenzenes (11 compounds)
- Phthalate esters (5 compounds)
- Phosphate triesters (5 compounds)
- PAHs (9 compounds)
- PCBs (10 compounds)
- Other quantitative compounds (19 compounds)
- Qualitative pesticides (9 compounds)
- Qualitative chlorinated aromatics (9 compounds)
- Qualitative PAHs (4 compounds)
- Other qualitative compounds (11 compounds)

Section 5.1.1 identifies the compounds analyzed within each chemical class and the detection percentages for each compound as observed within the NHATS FY86 composite samples. Statistical analysis was performed only on compounds with sufficiently high detection percentages. Section 5.1.2 discusses unique data reporting for two pesticides which have been historically prevalent in the NHATS program.

5.1.1 Detection Status of the Semivolatiles

When reporting a measured concentration for a given semivolatile compound in a laboratory sample, the NHATS FY86 analytical method determined whether the compound was successfully detected in the sample. For quantitative compounds, the method classified each result into one of three possible data qualifier categories, indicating the intensity of the signal response:

- Not detected -- Result is less than 2.5 times the signal-to-noise ratio.
- Trace -- Result is between 2.5 and 10 times the signal-to-noise ratio.
- Positive quantifiable -- Result is greater than 10 times the signal-to-noise ratio.

If a result was categorized as trace or positive quantifiable, the compound was considered detected in the sample. For qualitative compounds, only detected and not detected results were reported.

Estimated method detection limits were reported when not detected or trace results occurred for a sample. When a compound was not detected in a sample, it was assumed that the sample's true compound concentration was at some level below the detection limit. For the statistical analysis, one half of the detection limit was used as the estimated concentration level for not detected samples.

Table 5-1 reports the percentage of FY86 composite samples occurring in each of the data qualifier categories for the 111 semivolatile compounds. The percent of composite samples with detected results are also reported.

Of the 111 compounds, 23 were detected in at least 50% of the 50 composite samples, and one compound nearly met the 50% threshold (octachlorobiphenyl, detected in 44% of the samples). These 24 compounds are identified as *target compounds* for

Table 5-1. Percent of NHATS FY86 Composite Samples in Each Detection Level Category

	Compound Number and Name		CAS Number	% Detected	% Not Detected	% Trace	% Pos. Quant.
		PESTICIDES					
*	1	P,P-DDT	50-29-3	96	4	0	96
	2	O,P-DDT	789-02-6	0	100	0	0
*	3	P,P-DDE (M/Z=288)	72-55-9	100	0	0	100
*	3	P,P-DDE (M/Z=316)	72-55-9	100	0	0	100
	4	O,P-DDE	3424-82-6	0	100	0	0
	5	O,P-DDD	53-19-0	0	100	0	0
	6	ALPHA-BHC	319-84-6	0	100	0	0
*	7	BETA-BHC	319-85-7	92	8	2	90
	8	DELTA-BHC	319-86-8	0	100	0	0
	9	GAMMA-BHC(LINDANE)	58-89-9	4	96	0	4
	10	ALDRIN	309-00-2	0	100	0	0
	11	HEPTACHLOR	76-44-8	0	100	0	0
*	12	HEPTACHLOR EPOXIDE	1024-57-3	94	6	0	94
*	13	OXYCHLORDANE	26880-48-8	78	22	2	76
*	14	TRANS-NONACHLOR	39765-80-5	92	8	0	92
	15	GAMMA-CHLORDANE	57-74-9	0	100	0	0
	16	MIREX	2385-85-5	32	68	2	30
	60	DIELDRIN	60-57-1	12	88	0	12
*	60	DIELDRIN (CORRECTED)	60-57-1	62	38	22	40
	61	ENDRIN	7221-93-4	0	100	0	0
	62	ENDRIN KETONE		2	98	2	0
		CHLOROBENZENES					
	17	1,3-DICHLOROBENZENE	541-73-1	0	100	0	0
*	18	1,4-DICHLOROBENZENE	106-46-7	86	14	0	86
	19	1,2-DICHLOROBENZENE	95-50-1	0	100	0	0
	20	1,2,3-TRICHLOROBENZENE	87-61-6	0	100	0	0
	21	1,2,4-TRICHLOROBENZENE	120-82-1	0	100	0	0
	22	1,3,5-TRICHLOROBENZENE	108-70-3	0	100	0	0
	23	1,2,3,4-TETRACHLOROBENZENE	634-66-2	0	100	0	0
	24	1,2,3,5-TETRACHLOROBENZENE	634-90-2	0	100	0	0
	25	1,2,4,5-TETRACHLOROBENZENE	95-44-3	0	100	0	0
	26	PENTACHLOROBENZENE	608-93-5	0	100	0	0
*	27	HEXACHLOROBENZENE	118-74-1	98	2	4	94
		PAHs					
*	41	NAPHTHALENE	91-20-3	84	16	8	76
	42	ACENAPHTHALENE	208-96-8	0	100	0	0
	43	ACENAPHTHENE	83-32-9	0	100	0	0
	44	FLUORENE	86-73-7	0	100	0	0
	45	PHENANTHRENE	85-01-8	8	92	8	0
	46	FLUORANTHENE	206-44-0	2	98	2	0
	47	PYRENE	129-00-0	0	100	0	0
	48	CHRYSENE	218-01-9	4	96	0	4
	49	BENZO (A) PYRENE	50-32-8	0	100	0	0

Table 5-1. (cont.)

	Compound Number and Name		CAS Number	% Detected	% Not Detected	% Trace	% Pos. Quant.
		PCBs					
	50	MONOCHLOROBIPHENYL	2732-18-8	0	100	0	0
	51	DICHLOROBIPHENYL	25512-42-9	0	100	0	0
	52	TRICHLOROBIPHENYL	25323-68-6	30	70	2	28
*	53	TETRACHLOROBIPHENYL	26914-33-0	66	34	0	66
*	54	PENTACHLOROBIPHENYL	25429-29-2	88	12	0	88
*	55	HEXACHLOROBIPHENYL	26601-64-9	94	6	0	94
*	56	HEPTACHLOROBIPHENYL	28655-71-2	86	14	0	86
*	57	OCTACHLOROBIPHENYL	31472-83-0	44	56	0	44
	58	NONACHLOROBIPHENYL	53742-07-7	26	74	0	26
	59	DECACHLOROBIPHENYL	2051-24-3	28	72	0	28
		PHTHALATE ESTERS					
	63	DIMETHYL PHTHALATE	131-11-3	0	100	0	0
	64	DIETHYL PHTHALATE	84-66-2	10	90	2	8
*	65	DI-N-BUTYL PHTHALATE	84-74-2	76	24	6	70
*	66	BUTYL BENZYL PHTHALATE	85-68-7	72	28	4	68
*	67	BIS (2-ETHYLHEXYL) PHTHALATE	177-81-7	78	22	0	78
		PHOSPHATE TRIESTERS					
	68	TRIBUTYL PHOSPHATE	126-73-8	0	100	0	0
	69	TRIS (2-CHLOROETHYL) PHOSPHATE	115-96-8	0	100	0	0
	70	TRIS (2,3-DIBROMOPROPYL) PHOSPHATE	126-72-7	0	100	0	0
	71	TRIPHENYL PHOSPHATE	115-86-6	4	96	0	4
	72	TRITOLYL PHOSPHATE	1330-78-5	2	98	2	0
		OTHER					
	28	BIPHENYL	92-52-4	0	100	0	0
	29	1,2-DIBROMO-3-CHLORO PROPANE	96-12-8	0	100	0	0
	30	HEXACHLORO BUTADIENE	87-68-3	0	100	0	0
	31	HEXACHLORO CYCLOPENTADIENE	77-47-4	0	100	0	0
	32	2,2',4',5-TETRABROMO BIPHENYL		0	100	0	0
*	33	O-CYMENE	527-84-4	80	20	4	76
*	34	D-LIMONENE	5898-27-5	96	4	2	94
	35	D,L-ISOBORNEOL	124-76-5	0	100	0	0
	36	1-INDANONE	83-33-0	0	100	0	0
	37	2-INDANONE	615-13-4	0	100	0	0
	38	BUTYLATED HYDROXYTOLUENE	128-37-0	18	82	4	14
	39	COUMARIN	91-64-5	0	100	0	0
*	40	OCTAMETHYL-CYCLOTETRASILOXANE	556-67-2	72	28	4	68
	73	ETHYL HYDROCINNAMATE	2021-28-5	2	98	2	0
	74	2-METHOXY-3-METHYLPYRAZINE	2847-30-5	0	100	0	0

Table 5-1. (cont.)

	Compound Number and Name	CAS Number	% Detected	% Not Detected	% Trace	% Pos. Quant.
	OTHER (cont.)					
75	2,2',4,4',5-PENTACHLORO DIPHENYL ETHER		0	100	0	0
76	4-CHLORO-P-TERPHENYL		0	100	0	0
77	TRICHLORO-P-TERPHENYL		0	100	0	0
78	2-PHENYL PHENOL	90-43-7	24	76	2	22
	PESTICIDES (QUALITATIVE)[a]					
85	ISOPHORONE	78-59-1	16	84	-	-
86	DICHLOROVOS	62-73-7	2	98	-	-
98	CHLORPYRIFOS	2921-88-2	28	72	-	-
99	ISOPROPALIN	33820-53-0	10	90	-	-
100	BUTACHLOR	23184-66-9	12	88	-	-
101	NITROFEN	1836-75-5	8	92	-	-
102	PERTHANE	72-56-0	0	100	-	-
106	DICOFOL	115-32-2	6	94	-	-
107	P.P'-METHOXYCHLOR	72-43-5	0	100	-	-
	CHLORINATED AROMATICS (QUALITATIVE)[a]					
88	2,4,6-TRICHLOROANISOLE	87-40-1	0	100	-	-
89	2,4,6-TRICHLOROPHENOL	88-06-2	0	100	-	-
90	2,4,5-TRICHLOROPHENOL	95-95-4	0	100	-	-
91	2,3,6-TRICHLOROANISOLE	50375-10-5	0	100	-	-
92	2,3,6-TRICHLOROPHENOL	933-75-5	0	100	-	-
95	PENTACHLOROANISOLE		2	98	-	-
96	PENTACHLORONITROBENZENE	82-68-8	0	100	-	-
97	2,3,4-TRICHLOROANISOLE	54135-80-7	4	96	-	-
110	OCTACHLORONAPHTHALENE	2234-13-1	2	98	-	-
	PAHs (QUALITATIVE)[a]					
105	BENZO (A) ANTHRACENE	56-55-3	26	74	-	-
108	BENZO (B) FLUORANTHENE		10	90	-	-
109	BENZO (K) FLUORANTHENE	207-08-9	4	96	-	-
111	DIBENZO (A,H) ANTHRACENE	53-70-3	0	100	-	-
	OTHER (QUALITATIVE)[a]					
* 79	1-NONENE	124-11-8	50	50	-	-
80	CUMENE	98-82-8	34	66	-	-
* 81	1,2,4-TRIMETHYLBENZENE	95-63-6	62	38	-	-
* 82	HEXYL ACETATE	142-92-7	82	18	-	-
83	1,3-DIETHYLBENZENE	141-93-5	8	92	-	-
84	1,4-DIETHYLBENZENE	105-05-5	0	100	-	-
87	QUINOLINE	91-22-5	8	92	-	-
93	DIBENZOFURAN	132-64-9	0	100	-	-
94	CHLORDANE		2	98	-	-

Table 5-1. (cont.)

Compound Number and Name	CAS Number	% Detected	% Not Detected	% Trace	% Pos. Quant.
OTHER (QUALITATIVE) (cont.)					
103 CHLOROBENZYLATE	510-15-6	0	100	-	-
104 BIS (2-ETHYLHEXYL) ADIPATE	103-23-1	10	90	-	-

* Detected in at least 44% of the FY86 composite samples.

(a) Qualitative compounds were only monitored for detection versus non-detection.

statistical analysis and are noted with asterisks in Table 5-1. Statistical analysis of QC and composite data was restricted to these target compounds. For the other 87 compounds, each having no more than a 34% detection rate, results were summarized through descriptive statistics only.

5.1.2 Data Reporting Unique to Dieldrin and p,p-DDE

For two pesticides analyzed in the NHATS FY86 program, two sets of measured concentrations were obtained from different protocols. The two sets of results for these compounds, dieldrin and p,p-DDE, were each treated as two distinct entities in data analysis. The procedures unique to these compounds to obtain measured concentrations are discussed in this subsection.

According to Table 5-1, dieldrin had only a 12% detection rate among the FY86 composite samples. In Batches 1, 3, 4, and 5, the reported concentration levels for 29 samples (including 4 QC samples) were below the lowest calibration standard. According to the QAPP for laboratory analysis (MRI, 1988b), if the calculated laboratory response was below the range of calibration standards while satisfying criteria for retention time and ion ratio agreement, the value was to be identified as a "not detected" result. While this approach was followed for the initial set of reported dieldrin results, the HRGC/MS results indicated that dieldrin was indeed present in some samples whose measured concentrations were below the calibration standards. Thus the data qualifier classification of dieldrin data was redetermined to reflect the signal-to-noise ratio that would have been applied if the data were above the lowest calibration standard. The quantifiable concentrations for these samples were recalculated using the signal-to-noise ratio to define the detection limit. This second classification of the dieldrin data resulted in a 62% detection rate among the composite samples, classifying dieldrin as a target compound for statistical analysis. Thus statistical analysis for dieldrin was performed only on the recalculated results.

Historically, the compound p,p-DDE has been detected in a majority of NHATS samples. However, in the FY86 analysis, the primary quantitation ion used to calculate the p,p-DDE concentrations (m/z=288) was saturated at the mass spectrometry detector. It is expected that using an ion for quantitation at or near saturation would result in an underestimate of the true concentration. To help remedy this situation, a second set of p,p-DDE concentrations was calculated based on a lower response ion (m/z=316). The modified p,p-DDE data were obtained based on recalculated calibration curves. Unless interferences were present under the lower response ion, most of the modified data were higher than the original data based on the primary quantitation ion. Although the modified p,p-DDE data values are likely more accurate estimates of the true sample concentrations, most of these values were higher than the highest calibration standard. This caveat should accompany any conclusions made on the reported p,p-DDE data from the FY86 NHATS.

5.2 JUSTING CONCE TRATION DATA FOR OG T RECOVERI

Measured compound concentrations in NHATS composite samples are generally contaminated by systematic and random errors. A potential source of systematic error in the NHATS FY86 data has been identified by the recoveries of surrogate compounds spiked into the composite samples. These recoveries were much higher in FY86 compared with previous surveys. This type of systematic error can lead to the conclusion that measured concentrations for a compound are increasing over time, when in fact the true concentration has remained constant during the period.

Statistical methods for characterizing trend in compound concentrations should focus on how the true concentration changes over time rather than how the average measured concentration changes. Dinh (1991) has developed a statistical technique to estimate true concentration levels in the NHATS. This technique used the recoveries of surrogate

compounds to adjust the measured concentration data of native compounds. The result is a more accurate representation of the true concentration of native compounds over time. The NHATS statistical analyses summarized in this report, including trends analyses, were conducted on FY82, FY84, and FY86 data that were first adjusted by applying this technique. A discussion of this technique follows.

5.2.1 Data Adjustment Method

The statistical technique developed by Dinh (1991) for adjusting native compound concentrations was based on fitting a systematic errors-in-variables model to the NHATS data (see Sections 5.2.1.1 and 5.2.1.2). This model predicted the measured concentration as a linear function of the unknown true concentration. In turn, the expected value of the unknown true concentration given the measured concentration was estimated from the model fit. This latter result was considered an "adjustment" to the measured concentration and provided a more accurate estimate of the unknown actual concentration.

To estimate the expected value of an unknown true concentration in a composite sample, it was necessary to obtain accurate characterizations of recoveries and true concentrations for the native compounds. This information was best represented by analysis results on surrogate compounds. As part of the daily QC procedure, several surrogate compounds were injected at known concentrations into each NHATS composite sample. Surrogate compounds do not naturally exist in composite samples; thus the actual concentration of a surrogate compound in a sample is known to equal to the amount spiked into the sample. As a result, the recovery levels for surrogate compounds provided information on overall method performance and accuracy.

While recovery data were available for native compounds as well as surrogate compounds, only recoveries for surrogate compounds were used to adjust the measured concentrations of native compounds. Native compound recoveries were excluded for

the following reasons:

- native compound recoveries can be affected by contamination and interferences of unknown magnitude,
- native compound recoveries were available only for the 15 spiked QC samples, while surrogate recoveries were available for all NHATS samples.

Each surrogate compound spiked into an NHATS composite sample represented a class of one or more native compounds of interest. The surrogate compounds and the native compounds represented by each surrogate are listed in Table 5-2. When possible, a native compound was linked directly to its surrogate counterpart, such as lindane and chrysene. However, most native compounds did not have a direct surrogate counterpart included in the spiking. These compounds were associated with an average result across multiple surrogates in the relevant chemical group.

The methods used to adjust the measured concentrations of composite and QC samples are now discussed.

5.2.1.1 Composite Data Adjustment. In this procedure, the measured concentration of a compound is assumed to be linearly related to the actual compound concentration in a composite sample. Let C be the number of NHATS composite samples analyzed, let Y_i be a measured concentration of a compound in the i^{th} NHATS composite sample (i=1,...,C), and let μ_i be the compound's unknown true concentration in the sample. Then

$$Y_i = R\mu_i + e_i \quad , \tag{5-1}$$

where R is the unknown recovery of the compound by the analytical method, and e_i is random error having mean zero. Assume that μ_i and e_i are normally distributed and are uncorrelated across the composites. Then the expectation of μ_i given Y_i is given by

Table 5-2. Matching NHATS FY86 Native Compounds with Surrogate Compounds

Surrogate Compound[1]	ID Numbers of Native Compounds Linked with This Surrogate[2]
Chrysene-d_{12}	41-49
1,2,4-Trichlorobenzene-d_3	20-22
$^{13}C_6$ - 1,2,4,5-Tetrachlorobenzene	23-25
$^{13}C_6$ - Hexachlorobenzene	27
Mean of above three surrogates	17-19, 26
$^{13}C_6$ -4-Chlorobiphenyl	50
$^{13}C_{12}$ - 3,3',4,4'-Tetrachlorobiphenyl	53
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	57
$^{13}C_{12}$ - Decachlorobiphenyl	59
Mean of above four surrogates	51, 52, 58
Mean of tetra- and octa-chlorobiphenyl surrogates	54-56
^{13}C - Heptachlor	12
Lindane-d_6	9
Mean of above two surrogates	1-8, 10-11, 13-16, 60-62, 85-86, 98-102, 106-107
Mean of all ten surrogates above	28-40, 63-84, 87-97, 103-105, 108-111

(1)

$$E(\mu_i \mid Y_i) = [(1 - A)E(Y_i) + A*Y_i] / R \ , \qquad (5\text{-}2)$$

where

$$A = R^2 \, Var(\mu_i) / Var(Y_i)$$

Thus the true concentration μ_i in the i^{th} composite sample (i=1,...,C) is estimated by substituting estimates of the unknown parameters A, R, and $E(Y_i)$ in equation (5-2).

The arithmetic mean of the observed Y_i across the 50 composite samples, denoted by $\overline{Y}$, serves as an estimate for $E(Y_i)$ in equation (5-2). Estimates for A and R were obtained by fitting the regression model in (5-1) to measured concentrations of surrogate compounds. Let μ_i be the concentration at which a surrogate compound is spiked into composite sample i, and let Y_i be the resulting measured concentration of the surrogate compound in the sample. Because μ_i represents a true concentration, the linear regression model in (5-1) was fit to the composite sample data to obtain a least-squares estimate ($\hat{R}$) of the recovery R for the surrogate compound. The "r-squared" value from the regression (the regression sum of squares divided by the total sum of squares) is the estimate ($\hat{A}$) for the adjustment coefficient A. Substituting these parameter estimates in equation (5-2) leads to an estimate of the actual concentration in the composite sample:

$$\hat{\mu}_i = [(1-\hat{A})\overline{Y} + \hat{A}Y_i] / \hat{R} \qquad (5\text{-}3)$$

Thus for a given composite sample, Formula (5-3) represents an adjustment to the measured concentration for a given semivolatile compound.

Table 5-3 lists the estimates of R and A for all compounds in the FY82, FY84, and FY86 NHATS for semivolatiles. For FY86, these estimates are based on only those composite samples with a wet weight of at least ten grams. This table shows the relatively high recoveries in FY86 for most surrogate compounds (values of $\hat{R}$ greater than one) compared with the other fiscal years. Meanwhile, the estimated recoveries were similar for FY82 and FY84.

Among the three fiscal years in Table 5-3, spiked and measured concentrations for surrogate compound data were only available for the FY84 and FY86 NHATS. Thus only for the FY84 and FY86 NHATS could the parameters R and A could be estimated by fitting the linear regression model in equation (5-1). In contrast, only recovery data were available for surrogate compounds in the FY82 NHATS. As a result, an estimate of R for a given surrogate compound in the FY82 NHATS was calculated by averaging the observed sample recoveries. Because an estimate of A could not be determined from the available FY82 surrogate data, the corresponding estimates of A from the FY84 data were applied to FY82.

5.2.1.2 QC Data Adjustment. A slight modification to the approach in 5.2.1.1 was needed to adjust the measured concentration of a native compound in an analytical sample when a portion of the concentration in the sample was known. This situation occurred when the sample was spiked with a known amount of the compound. For example, ten of the FY86 NHATS QC samples were spiked with 36 native compounds prior to analysis. The known portion of the concentration must be considered when estimating the entire actual compound concentration in the sample.

Suppose that the i^{th} QC sample was spiked with a native compound at a known concentration S_i. Let the unknown concentration of the native compound in this sample be μ_i before

Table 5-3. Estimates of R and A for Surrogate Compounds

Native Compound (or group of compounds)[1]	NHATS FY82[2]		NHATS FY84		NHATS FY86[3]	
	$\hat{R}$	$\hat{A}$	$\hat{R}$	$\hat{A}$	$\hat{R}$	$\hat{A}$
Pesticide group[4]						
Heptachlor epoxide	0.5764	0.9558	0.6069	0.9725	1.2761	0.9082
Lindane	0.5764	0.9558	0.6069	0.9725	0.9704	0.9120
All other pesticides[5]	0.5764	0.9558	0.6069	0.9725	1.1381	0.9292
Chlorobenzene group						
Trichloro-benzene	0.5089	0.8697	0.2915	0.8697	0.6203	0.9100
Tetrachloro-benzene	0.4374	0.9301	0.4400	0.9301	0.7666	0.9290
Hexachloro-benzene	0.5788	0.9716	0.5658	0.9716	0.9940	0.9413
Other Chloro-benzenes[6]	0.5089	0.9514	0.4325	0.9514	0.7586	0.9315
PAH group						
Chrysene and other PAH compounds	0.5858	0.9805	0.6500	0.9805	1.0088	0.9743
PCBs group						
Monochloro-biphenyl	0.6223	0.9584	0.6580	0.9584	1.0252	0.9453
Tetrachloro-biphenyl	0.6798	0.9552	0.6452	0.9552	1.2569	0.9306
Penta-, Hexa-, and Heptachloro-biphenyl[7]	0.5089	0.9696	0.6455	0.9696	1.2018	0.9154
Octachloro-biphenyl	0.4968	0.9662	0.6456	0.9662	1.1694	0.8975

Table 5-3. (cont.)

Native Compound (or group of compounds)[1]	NHATS FY82[2]		NHATS FY84		NHATS FY86[3]	
	$\hat{R}$	$\hat{A}$	$\hat{R}$	$\hat{A}$	$\hat{R}$	$\hat{A}$
Decachloro-biphenyl	0.6272	0.9022	0.6414	0.9022	1.0467	0.8618
Di-, Tri-, and Nonachloro-biphenyl[8]	0.6078	0.9679	0.6448	0.9679	1.1117	0.9120
Diethyl phthlate	0.5764	0.9032	0.6313	0.9032	1.0369	0.9340
Di-n-butyl phthalate	0.5764	0.7850	0.4472	0.7850	1.0369	0.9340
Butyl benzyl phthalate	0.5764	0.6145	0.4059	0.6145	1.0369	0.9340
Other phthalates	0.5764	0.8235	0.4948	0.8235	1.0369	0.9340
Other compounds	0.5764	0.9558	0.6637	0.9558	1.0369	0.9340

Notes for Table 5-3

(1) Grouping of compounds without direct surrogate counterparts for FY86 is documented in Table 5-2.

(2) **Estimates of A for FY82 are taken from FY84 estimates.**

(3) **Composite samples having ten or more grams wet weight were used in determining** estimates for R and A.

(4) Surrogates for pesticides were not analyzed in FY82 or FY84. Estimates for these two years are based on the linear regression in (5-1) where Y_i and μ_i are substituted by the average of the spiked and found concentrations across all surrogates.

(5) The estimates of R and A for FY86 are obtained by the linear regression in (5-1) where Y_i and μ_i are substituted by the average of the found and spiked concentrations, respectively, of surrogate heptachlor and lindane.

Table 5-3. (cont.)

(6) The estimates of R and A are obtained by the linear regression in (5-1) where Y_i and μ_i are substituted by the average of the found and spiked concentrations, respectively, of surrogate tri-, tetra-, and hexa-chlorobenzene.

(7) The estimates of R and A are obtained by the linear regression in (5-1) where Y_i and μ_i are substituted by the average of the found and spiked concentrations, respectively, of surrogate tetra- and octa-chlorobiphenyl.

(8) The estimates of R and A are obtained by the linear regression in (5-1) where Y_i and μ_i are substituted by the average of the found and spiked concentrations, respectively, of surrogate mono-, tetra-, octa-, and deca-chlorobiphenyl.

(9) Surrogates corresponding to phthalates were not analyzed in FY82. Surrogate phthalate data in FY86 were not analyzed due to the prevalence of missing values. Estimates of R and A for phthalates in FY82 and FY86 are based on the linear regression in (5-1) where Y_i and μ_i are substituted by the average of the spiked and found concentrations across all surrogates.

(10) Estimates of R and A for all compounds not represented on other rows of this table are based on the linear regression in (5-1) where Y_i and μ_i are substituted by the average of the spiked and found concentrations across all surrogates.

spiking and $\mu_i^* = \mu_i + S_i$ after spiking. Note that a portion of the unknown concentration μ_i^* is known. Similar to equation (5-1), the measured concentration Y_i^* of the i^{th} QC sample can be expressed as

$$Y_i^* = R\mu_i^* + e_i = R(\mu_i + S_i) + e_i \quad , \tag{5-4}$$

As in equation (5-2), the expectation of μ_i^* given Y_i^* is given by

$$E(\mu_i^* \mid Y_i^*) = [(1 - A)E(Y_i^*) + A*Y_i^*] / R \quad , \tag{5-5}$$

where A and R are as in equation (5-2). Thus the adjusted measured concentration for spiked samples is given by the following estimate of $E(\mu_i^* \mid Y_i^*)$:

$$\hat{\mu}_i^* = [(1-\hat{A})(B + \hat{R}S_i) + \hat{A}Y_i] / \hat{R} \tag{5-6}$$

where B is an estimate of the background concentration (discussed in the following paragraph), and $\hat{A}$ and $\hat{R}$ are as in formula (5-3). The last two columns of Table 5-3 contain the estimates $\hat{A}$ and $\hat{R}$ that were substituted in equation (5-6) for each compound.

The background sample concentration, represented by B in equation (5-6), was estimated by fitting a linear regression model. This model, labeled the *full batch effects model* in Section 5.3.2, estimates the linear relationship between the spiked concentration and the measured concentration in a spiked sample. This relationship was allowed to change according to the batch in which the sample was analyzed. This model has the following form:

$$Y_{ij} = \alpha_i + \beta_i S_J + e_{ij} \quad , \tag{5-7}$$

where Y_{ij}^* is the measured concentration for the j^{th} QC sample (j=1,2,3) in the i^{th} batch (i=1,...,5), S_j is the spike level of the j^{th} QC sample, and e_{ij} represents random error. The parameters α_i and β_i (i=1,...,5) represent batch intercepts and slopes, respectively. These parameters were estimated by fitting the model to the QC data. The average of the estimates for the five batch intercepts α_i (i=1,...,5) was taken as the value of B in formula (5-6).

Note that the modification presented in this subsection to adjust measured concentrations was relevant only when a native compound was spiked into the given sample. No modification was necessary for adjusting measured concentrations for unspiked native compounds in these samples.

5.3 STATISTICAL ANALYSIS OF QUALITY CONTROL DATA

The statistical analysis of quality control (QC) data was performed to meet a number of study objectives prior to composite data analysis. These objectives include:

- estimating the percent recovery of the analytical method for spiked compounds,
- determining if any significant differences exist in the analytical performance among the five batches,
- characterizing the precision of the analytical method,
- identifying estimates of measurement error present in the data within a batch,
- establishing the relationship in spiked compounds between the precision of the analytical method and the level of the spiked concentration,
- identifying anomalous results that suggest potential problems in the analytical measurements and which may cause removal of some of all data for a compound in further statistical analysis.

Of the seventy samples analyzed in the FY86 semivolatiles study, fifteen were QC samples, and five were method blanks. Each of the five analysis batches contained one method blank, one unspiked control sample, and two spiked samples (one sample spiked at a lower concentration than the other). The QC samples were prepared from a homogenized bulk lipid sample, allowing for comparisons in method quality to be made between batches.

Within a batch, the three lipid-based QC samples were randomized with the ten composite samples in determining the order of sample testing. The randomization ensured that no systematic trends due to changes in laboratory procedures were introduced into the analysis results. The method blank was the first sample analyzed within each batch.

A total of 36 compounds were spiked into the two spiked QC samples for each batch. The spiking levels and compounds were determined by MRI in consultation with the EPA/OPPT WAM. Sixteen of these compounds were identified in Section 5.1 as target compounds for statistical analysis. They are listed in Table 5-4 with their spike levels. These levels were multiplied by 200 (solutions were spiked in a 200 μL aliquot), then divided by the percent lipid weight (in grams) of the sample to obtain spike concentrations (ng/g) for the sample. QC analysis was performed on these spiked target compounds.

Eight additional compounds were identified in Section 5.1 as target compounds for statistical analysis, but they were not spiked into the QC samples. These compounds were identified as *unspiked target compounds*. The eight unspiked target compounds were:

- Beta-BHC
- Oxychlordane
- Naphthalene
- Di-N-Butyl phthalate
- Bis (2-Ethylhexyl) phthalate
- 1-Nonene
- 1,2,4-Trimethylbenzene
- Hexyl acetate

Table 5-4. Spiked Target Compounds for the FY86 NHATS, With Spiking Levels

Compound (ID and Name) (1)		Low Spike Level (ng/μL)	High Spike Level (ng/μL)
Pesticides			
1	p,p-DDT	5.28	21.1
3	p,p-DDE	7.38	29.5
12	Heptachlor Epoxide	3.58	14.3
14	Trans-nonachlor	5.48	21.9
60	Dieldrin(2)	5.48	21.9
Chlorobenzenes			
18	1,4-Dichlorobenzene	31.0	124.
27	Hexachlorobenzene	4.88	19.5
PCBs			
53	Tetrachlorobiphenyl	14.1	56.2
54	Pentachlorobiphenyl	16.3	65.0
55	Hexachlorobiphenyl	13.2	52.6
56	Heptachlorobiphenyl	32.5	130.
57	Octachlorobiphenyl	34.3	137.
Phthalate Esters			
66	Butyl Benzyl Phthalate	5.65	22.6
Other			
33	O-cymene	7.00	28.0
34	D-limonene	5.98	23.9
40	Octamethyl Cyclotetrasiloxane	5.28	21.1

(1) **All listed compounds except octachlorobiphenyl were detected in at least 50% of the NHATS FY86 composite samples.** Octachlorobiphenyl was detected in 44% of the samples.
(2) **Detected in > 50% of the NHATS FY86** composite samples when S/N calculation is used (see Section 5.1.2).

$$\text{Spike level (ng/g)} = \frac{\text{Spike level (ng/}\mu\text{L)} * 200\ \mu\text{L}}{\text{Percent lipid weight (g)}}$$

Source: Table 9 of MRI Batch Reports (updated 8/10/90)

QC data analysis for these target compounds was limited to identifying effects due to batch and to QC sample type. Thus QC analysis was performed on a total of 24 of the FY86 semivolatile compounds.

If a compound was not detected in a QC sample, the measured concentration was computed as one-half of the detection limit. This same approach was used in the statistical analysis of the composite samples.

A listing of the QC data, both unadjusted and adjusted for surrogate recoveries, is found in Appendix B. All QC analysis was performed on data adjusted for surrogate recoveries.

5.3.1 Descriptive Summary of QC Data

5.3.1.1. Spiked Compounds. Table 5-5 contains a summary of the QC data for the 16 spiked target compounds. The data are corrected for surrogate recoveries as discussed in Section 5.2. Presented for each target compound and each of the four QC sample types are the following statistics:

- the number of samples with reported results,
- the number of detected results,
- the average and standard deviation of the observed concentrations (ng/g),
- the coefficient of variation (%), equal to the standard deviation divided by the average.

For the spiked samples, the following recovery information is also presented:

- the average spike level (ng/g),
- the background average recovery (%), calculated as the average (across batches) of the following ratio:

Table 5-5. Summary of (Surrogate-Adjusted) QC Data for the FY86 NHATS Spiked Target Compounds

Compound	Spike Level	# Samples	# Detected	Avg. Spike Level (ng/g)	Avg. Observed Conc. (ng/g)	Background Adjusted Recovery (%)	Std. Dev. of Conc. (ng/g)	C.V. (%)
p,p-DDT	MB	5	0	-	3.33	-	1.43	42.85
	Control	5	5	0.00	211.09	-	17.56	8.32
	Low	5	5	53.32	262.38	95.91	34.44	13.12
	High	5	5	212.27	470.24	122.24	71.75	15.26
p,p-DDE (m/z=288)	MB	5	0	-	3.57	-	1.40	39.23
	Control	5	5	0.00	2979.26	-	1183.27	39.72
	Low	5	5	74.53	2721.64	-343.59	1371.98	50.41
	High	5	5	296.77	2877.80	-33.97	1627.77	56.56
p,p-DDE (m/z=316)	MB	0	0	-	-	-	-	-
	Control	5	5	0.00	2735.68	-	1356.11	49.57
	Low	5	5	74.53	2606.68	-174.00	1364.86	52.36
	High	5	5	296.77	2667.58	-22.63	1688.32	63.29
Heptachlor epoxide	MB	5	0	-	3.42	-	1.34	39.12
	Control	5	5	0.00	92.59	-	21.34	23.05
	Low	5	5	36.15	135.53	118.31	25.28	18.65
	High	5	5	143.86	221.71	89.75	45.83	20.67
Trans-nonachlor	MB	5	0	-	3.50	-	1.37	39.12
	Control	5	5	0.00	238.12	-	125.99	52.91
	Low	5	5	55.34	236.32	-1.94	70.05	29.64
	High	5	5	220.32	350.87	51.15	164.24	46.81

Table 5-5. (cont.)

Compound	Spike Level	# Samples	# Detected	Avg. Spike Level (ng/g)	Avg. Observed Conc. (ng/g)	Background Adjusted Recovery (%)	Std. Dev. of Conc. (ng/g)	C.V. (%)
Dieldrin (corrected)	MB	0	0	-	-	-	-	-
	Control	4	5	0.00	56.19	-	47.78	85.04
	Low	4	5	55.34	103.41	85.34	84.31	81.53
	High	5	5	220.32	164.33	49.18	102.60	62.44
1,4-Dichlorobenzene	MB	5	0	-	3.01	-	1.17	39.06
	Control	5	5	0.00	177.05	-	63.57	35.90
	Low	5	5	313.06	266.77	29.10	130.45	48.90
	High	5	5	1247.5	875.60	56.03	256.10	29.25
Hexachlorobenzene	MB	5	0	-	3.43	-	1.34	39.07
	Control	5	5	0.00	71.51	-	4.04	5.66
	Low	5	5	49.28	118.76	95.78	21.91	18.45
	High	5	5	196.17	284.30	108.49	22.98	8.08
Tetrachlorobiphenyl	MB	5	0	-	4.00	-	0.00	0.00
	Control	5	4	0.00	85.59	-	28.23	32.98
	Low	5	5	142.39	208.41	86.30	55.16	26.47
	High	5	5	565.38	580.71	87.67	132.29	22.78
Pentachlorobiphenyl	MB	5	0	-	8.60	-	0.00	0.00
	Control	5	5	0.00	194.01	-	92.02	47.43
	Low	5	5	164.61	321.57	77.38	165.68	51.52
	High	5	5	653.91	702.98	78.01	260.33	37.03

Table 5-5. (cont.)

Compound	Spike Level	# Samples	# Detected	Avg. Spike Level (ng/g)	Avg. Observed Conc. (ng/g)	Background Adjusted Recovery (%)	Std. Dev. of Conc. (ng/g)	C.V. (%)
Hexachlorobiphenyl	MB	5	0	-	8.90	-	0.00	0.00
	Control	5	5	0.00	1042.11	-	78.08	7.49
	Low	5	5	133.31	1044.40	1.43	61.89	5.93
	High	5	5	529.16	1282.64	45.40	70.49	5.50
Heptachlorobiphenyl	MB	5	0	-	9.15	-	0.00	0.00
	Control	5	5	0.00	679.24	-	147.79	21.76
	Low	5	5	328.21	976.65	90.56	110.02	11.27
	High	5	5	1307.8	1743.22	81.49	362.28	20.78
Octachlorobiphenyl	MB	5	0	-	8.90	-	0.00	0.00
	Control	5	5	0.00	142.68	-	64.48	45.19
	Low	5	5	346.39	531.73	111.94	130.41	24.53
	High	5	5	1378.2	1537.61	101.36	468.91	30.50
Butyl benzyl phthalate	MB	4	2	-	13.30	-	11.35	85.31
	Control	5	3	0.00	36.63	-	29.38	80.20
	Low	5	4	57.06	104.33	119.06	53.64	51.42
	High	5	5	227.36	180.83	63.55	110.33	61.02
O-cymene	MB	5	0	-	3.57	-	1.40	39.12
	Control	5	3	0.00	11.04	-	6.09	55.15
	Low	5	3	70.69	12.82	2.63	4.00	31.18
	High	5	5	281.68	59.59	17.26	38.76	65.05

Table 5-5. (cont.)

Compound	Spike Level	# Samples	# Detected	Avg. Spike Level (ng/g)	Avg. Observed Conc. (ng/g)	Background Adjusted Recovery (%)	Std. Dev. of Conc. (ng/g)	C.V. (%)
D-limonene	MB	5	2	-	11.52	-	11.55	100.24
	Control	5	5	0.00	122.24	-	40.19	32.88
	Low	5	5	60.39	108.62	-21.45	52.65	48.48
	High	5	5	240.44	223.09	41.94	53.90	24.16
Octamethyl-cyclotetrasiloxane	MB	5	1	-	34.59	-	67.89	196.27
	Control	5	2	0.00	8.03	-	6.15	76.62
	Low	5	2	53.32	10.28	4.30	4.17	40.61
	High	5	4	212.27	66.84	27.73	38.34	57.35

$$Recovery(\%) = \frac{conc.\ (spiked\ sample) - conc.\ (control\ sample)}{Spike\ level} * 100 \quad (5\text{-}8)$$

Table 5-5 shows that the higher spike level for p,p-DDE was approximately ten percent of the average background level given by the control sample. The laboratory analysis was unable to estimate recoveries for p,p-DDE due to the high background level relative to the spiking levels. As a result, estimated background-adjusted recoveries (BARs) for p,p-DDE were negative. BARs near zero were observed at low spike levels for trans-nonachlor, hexachlorobenzene, and D-limonene, all as a result of high background levels.

BARs of less than 50% were observed for o-cymene, D-limonene, and octamethyl-cyclotetrasiloxane, despite spike levels generally above observed background. Thus these three compounds may have recovery problems. The BAR for 1,4-Dichlorobenzene was less than 60%, reflecting the higher volatility in this compound compared to the other target compounds. Except for hexachlorobiphenyl (which had low recoveries), the BARs for PCBs ranged from 77 to 112 percent. For p,p-DDT, heptachlor epoxide, hexachlorobenzene, and butyl benzyl phthalate, the BARs ranged from 64 to 122 percent.

The "BAR" approach to calculating percent recoveries given in equation (5-8) has been recommended for use through the NHATS program. However, an alternative approach to calculating percent recoveries does not place as much emphasis on the ability to detect finite differences in concentration. This approach considers the formula

$$Recovery(\%) = \frac{conc.\ (spiked\ sample)}{conc.\ (control\ sample) + spike\ level} * 100\% \quad (5\text{-}9)$$

Note that the percentages calculated from (5-9) are always positive and are equal to 100% when the observed concentration equals the sum of the spike level and the control sample concentration within the batch. Table 5-6 presents the percent recoveries under both approaches (5-8) and (5-9) for the spiked target compounds. In this setting, approach (5-9) generally leads to improved percent recovery values over approach (5-8). This is especially apparent with p,p-DDE, where the spike levels were much smaller than the observed levels in the control samples. While approach (5-8) has been recommended for the NHATS program, both approaches evaluate method performance differently, and thus both sets of results should enter into performance evaluation.

Coefficients of variation were widely varied among the samples and compounds (Table 5-5). Only p,p-DDT, heptachlor epoxide, hexachlorobenzene, hexachlorobiphenyl, and heptachlorobiphenyl had coefficients of variation which were at 25% or smaller for all samples. For the other spiked target compounds, the variation in the QC results at a given spike level was as high as 80% of the observed average level across the batches.

For dieldrin, butyl benzyl phthalate, o-cymene, and octamethyl-cyclotetrasiloxane, at least one QC sample result was not detected at the low spike level.

Appendix C contains plots of the measured concentrations versus the spike levels for all study compounds. Although some plots indicate a linear increasing relationship, most plots show highly variable results among the batches at a given spike level. Several of the plots suggest that concentrations were higher for Batches 4 and 5 than for the other three batches, such as with p,p-DDT, p,p-DDE, and some of the PCBs. This was especially evident at high spike levels.

Appendix D contains summaries like those in Table 5-5 for spiked compounds not on the target list.

Table 5-6. Percent Recoveries for Spiked Target Compounds, as Determined from Two Calculation Methods

Compound	% Recovery Using Equation (5-8)		% Recovery Using Equation (5-9)	
	Low spike	High spike	Low spike	High spike
p,p-DDT	95.91	122.24	98.95	110.86
p,p-DDE (m/z=288)	-343.59	-33.97	88.27	82.30
p,p-DDE (m/z=316)	-174.00	-22.63	97.32	80.57
Heptachlor epoxide	118.31	89.75	105.38	93.66
Trans-nonachlor	-1.94	51.15	84.27	79.83
Dieldrin (corrected)	85.34	49.18	84.99	56.90
1,4-Dichlorobenzene	29.10	56.03	55.81	61.26
Hexachlorobenzene	95.78	108.49	98.60	106.33
Tetrachlorobiphenyl	86.30	87.67	91.50	89.00
Pentachlorobiphenyl	77.38	78.01	98.01	83.27
Hexachlorobiphenyl	1.43	45.40	89.04	81.71
Heptachlorobiphenyl	90.56	81.49	97.43	88.14
Octachlorobiphenyl	111.94	101.36	109.92	101.17
Butyl benzyl phthalate	119.06	63.55	110.52	66.72
O-cymene	2.63	17.26	15.81	20.35
D-limonene	-21.45	41.94	64.29	61.94
Octamethyl-cyclotetrasiloxane	4.30	27.73	17.02	30.11

Two methods to calculating percent recovery on the surrogate-adjusted data:

$$\text{Recovery}(\%) = \frac{\text{conc. (spiked sample)} - \text{conc. (control sample)}}{\text{Spike level}} * 100\% \quad (5\text{-}8)$$

$$\text{Recovery}(\%) = \frac{\text{conc. (spiked sample)}}{\text{conc. (control sample)} + \text{spike level}} * 100\% \quad (5\text{-}9)$$

5.3.1.2 Unspiked Compounds. Table 5-7 contains descriptive summaries of eight target compound concentrations that were not spiked in the control samples. The descriptive statistics were calculated for each batch and across all batches.

5.3.1.3. Method Blanks. Method blanks were used to assess laboratory background contribution to concentration levels within the composite samples. Eight of the target compounds were detected in the method blanks. When detectable concentrations were measured in method blanks, the results are presented in Table 5-8. Detection in the method blanks suggests a potential bias in the reported concentration levels within the affected batches for the given compound.

The method blanks for Batches 1 and 5 had detectable levels for the three target phthalates. The bis (2-ethylhexyl) phthalate was also detected in the method blank for Batch 3. The method blank for Batch 4 was not analyzed for phthalates. In most cases, the method blank concentration was at or above the control (unspiked) sample, suggesting laboratory background contribution to the measured concentration.

5.3.2 Statistical Approach to Analyzing the QC Data

To address the statistical objectives presented at the beginning of Section 5.3, the QC data were statistically analyzed using linear models fitted to the surrogate-adjusted concentrations for each compound. A linear regression model was applied to concentration data for spiked compounds. This model included effects for batch and spike level. A similar analysis of variance application determined whether batch and sample type effects were statistically significant on concentrations for unspiked compounds. The statistical methods and results are described in this subsection.

5.3.2.1 Spiked Compounds. Two types of linear regression models were fit to the QC data for spiked target compounds. One model,

Table 5-7. Means and Standard Errors of Surrogate-Adjusted Concentrations (ng/g) of Unspiked Target Compounds for QC Samples (By Batch and Overall)

Compound	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	All Batches
Beta-BHC	147.04 (66.01)	261.88 (121.63)	126.33 (108.90)	310.39 (8.11)	221.18 (89.94)	213.364 (38.198)
Oxychlordane	12.43 (0.02)	94.07 (40.89)	132.41 (9.57)	146.56 (11.32)	143.84 (7.79)	105.864 (15.389)
Naphthalene	11.40 (3.22)	8.63 (1.93)	6.24 (3.62)	11.71 (0.61)	10.68 (0.59)	9.731 (1.048)
Di-n-butyl phthalate	23.70 (10.18)	44.36 (17.06)	12.28 (1.37)	62.32 (5.69)	56.31 (21.91)	39.795 (7.205)
Bis (2-ethylhexyl) phthalate	414.00 (330.21)	231.36 (147.34)	191.66 (63.43)	78.96 (39.24)	629.34 (456.20)	309.065 (111.818)
1-Nonene	360.11 (79.44)	218.99 (175.67)	513.24 (237.20)	720.42 (108.26)	447.18 (247.80)	451.988 (82.086)
1,2,4 -Trimethylbenzene	18.14 (10.32)	62.43 (21.65)	21.14 (8.26)	63.18 (29.27)	15.14 (7.39)	36.005 (8.882)
Hexyl acetate	68.01 (15.01)	158.83 (107.74)	137.82 (115.44)	179.10 (94.90)	59.00 (3.00)	120.552 (33.826)

Standard errors are in parentheses beneath the means.

These statistics represent three lipid-based QC samples (C, S1, S2) per batch. All act as control samples for unspiked compounds.

Table 5-8. Batch Analysis Results on Method Blanks and Control Samples for Compounds Detected in At Least 50% of Composites, where the Compound Was Detected in the Method Blank

Compound	Batch	Lab #	Conc. of Method Blank (ng/g)	Conc. of Control Sample (ng/g)	% of Control Conc.
Phthalate Esters					
Di-n-butyl phthalate	1	17901	44.9	12.05	373.
	5	17957	13.7	20.2	67.8
Butyl benzyl phthalate	1	17901	29.1	10.55	276.
	5	17957	14.0	13.7	102.
Bis (2-ethylhexyl) phthalate	1	17901	205.	57.8	355.
	2	17915	581.	560.	104.
	3	17929	288.	222.	130.
	5	17957	15.4	348.	4.4
Other					
D-limonene	2	17915	27.9	85.4	32.7
	5	17957	19.5	164.	11.9
Octamethyl-cyclotetrasiloxane	3	17929	156.	20.3	768.
Other (qualitative)					
1-nonene	1	17901	600.	200.	300.
	2	17915	1000.	600.	167.
1,2,4-trimethylbenzene	3	17929	40.0	30.0	133.
Hexyl acetate	1	17901	20.0	50.0	40.0
	3	17929	400.	2.50	16000

Note: Concentrations are unadjusted for surrogate recoveries.

known as the *batch slopes model*, provided estimates of batch recoveries and tests for equality of these estimates across batches. The other model, called the *batch intercepts model*, was considered when spiked sample results were not sufficiently above background to allow for batch recovery estimates to be made. The batch intercepts model provided for separate background levels to be estimated for each batch. These models are summarized in Table 5-9 and satisfactorily characterize the FY86 QC data for all compounds.

The *full batch effects model* introduced in Section 5.2.1 and presented in (5-7) was also considered in this application. The full batch effects model, a composite of the batch slopes and batch intercepts models, contains ten parameters which represent separate slopes and intercepts for the five batches. This is a large number of parameters compared with the number of data points (15), leading to overparametrization problems. When either constant batch backgrounds or constant batch slopes cannot be assumed, a *simple linear regression model*, with constant background and slope across batches, was considered.

The batch slopes model tested for significant differences in batch recoveries for the spiked compound. This model also estimated the batch recoveries and the average recovery across all batches, and calculates predicted concentrations at each spike level. The average recovery was tested for significant difference from 100%, thus determining the accuracy of the analytical method. The estimated intercept term was interpreted as the estimate of background (or systematic error) across all batches. Batch effects were present when at least one of the estimated slopes was found to be significantly different from the others.

According to the descriptive results presented earlier in this section, the spike levels for some compounds were low relative to background. Thus the reported concentrations for spiked samples were at the background level. This outcome was

Table 5-9. Regression Models Used to Analyze NHATS FY86 QC Data for Spiked Compounds

Model	Equation[1]	Model interpretation
Batch Slopes Model	$EC_{ij} = \alpha + \beta_i * SC_j$	Intercept (α) represents the background level across all batches. Slopes (β_i, i=1,2,...,5) represent the batch recoveries. When data are balanced[2], the average of the estimated batch recoveries from this model equals the slope which would have been fitted if batch was not represented in the model.
Batch Intercepts Model	$EC_{ij} = \alpha_i + \beta * SC_j$	Intercepts (α_i, i=1,2,...,5) represent the batch background levels. When data are balanced[2], the average of the estimated batch background levels from this model equals the intercept which would have been fitted if batch was not represented in the model. Slope (β) represents the estimated recovery across all batches.

[1] EC_{ij} = Expected compound concentration (ng/g) in the jth QC sample of batch i (i=1,2,...,5; j=1 (Control),2 (low spike), 3(high spike))
SC_j = Spike levels of the jth QC sample (j=1 (Control), 2 (low spike), 3 (high spike))

[2] In this application, the data are balanced whenever there are equal numbers of control, low spike, and high spike samples with reported data.

observed for p,p-DDE. A batch slopes model was not appropriate in this situation, as batch recoveries cannot be estimated from the observed data. Affected compounds were analyzed using the batch intercepts model or simple linear regression model to note overall differences among batches.

The statistical analysis of QC data established that significant batch effects existed in the data for virtually all spiked target compounds. Specifically, estimated recoveries for Batches 4 and 5 tended to differ from the first three batches. As a result, all statistical analyses on composite samples included a "batch class" effect (Batches 1-3 versus 4-5). Any batch effects existing beyond the "batch class" effect were treated as random effects.

The NHATS additive model assumes that the standard deviation of the measured concentration in composite samples has two components:

- a component associated with the within-batch measurement error, estimated by the mean-squared error (MSE) from the batch slopes model,
- a random component associated with the random-batch effects within each batch "class".

For a spiked target compound, the predicted average concentration at the j^{th} spiked concentration SC_j (j = 1, 2) is given by

$$\hat{C}_j = \hat{\alpha} + \hat{\beta}_{avg} * SC_j \,, \qquad (5\text{-}10)$$

where $\hat{\alpha}$ is the baseline average concentration and $\hat{\beta}_{avg}$ is the average estimated recovery across batches. Note that $\hat{\alpha}$ is the least-squares estimate of the parameter α and $\hat{\beta}_{avg}$ is the average of the least squares estimates of β_i, both resulting from fitting the batch slopes model in Table 5-9. The standard deviation of $\hat{C}_j$ is computed as

$$SD(\hat{C}_j) = \sqrt{MSE + SC_j * SD(\beta)}\ , \qquad (5\text{-}11)$$

where MSE is the mean-squared error from the batch slopes model, and $SD(\beta)$ is the sample standard deviation of the estimated batch recoveries. Thus the standard deviation increases with the concentration of the sample; however, it is not necessarily proportional to the concentration. If the batch slopes model indicated that a significant batch effect existed, only recoveries from Batches 1-3 were used to estimate the parameters $\hat{\beta}_{avg}$ and $SD(\beta)$. Otherwise all five batches were used.

5.3.2.2 Unspiked Compounds. Although batch recoveries could not be estimated for the eight unspiked target compounds, batch effects and method contamination could still be characterized for these compounds. A two-way analysis of variance approach was applied to these compounds containing effects representing the batch and the sample type (control, low spike, high spike). The batch effect provided a test for significant differences in concentrations between batches. The effect for sample type allowed for tests between samples containing different spiking solutions. This latter test was a means of determining the presence of method contamination.

5.3.3 Results of Statistical Modelling of QC Data

5.3.3.1 Spiked Compounds. The results of fitting the batch slopes model in Table 5-9 to the QC data for spiked target compounds are summarized in Tables 5-10 through 5-12. Table 5-10 contains the estimated batch recoveries for each spiked target compound, as well as the estimated average recovery across all batches. Table 5-11 reports significance levels for tests of equal recoveries among sets of batches. Table 5-12 provides information on observed precision.

Table 5-10 Estimated Batch Recoveries and Average Recovery for Spiked Compounds with Percent Detected At Least 50% (Adjusted Data)

Compound	Estimated Average Recovery (%)	S.E.[2]	Estimated Batch Recoveries (%)[1]					Sig. Batch Slope Effect?
			1	2	3	4	5	
p,p-DDT	124*	5.4	108	90.2	97.8	170	156	Yes
p,p-DDE (m/z=288)	-6.60	213	---	---	---	---	---	---
p,p-DDE (m/z=316)	-7.83	229	---	---	---	---	---	---
Heptachlor epoxide	87.8*	9.08	63.2	71.8	58.7	122	123	Yes
Trans-nonachlor	56.0*	27.4	58.9	-53.1	40.0	121	117	No
Dieldrin (modified)	46.2*	14.3	-15.9	42.5	60.8	19.4	124	Yes
1,4-Dichlorobenzene	58.1*	4.83	32.0	59.7	43.5	72.1	83.1	Yes
Hexachlorobenzene	110*	3.91	95.6	111	97.3	127	117	Yes
Tetrachlorobiphenyl	87.8*	2.81	64.2	73.7	72.1	113	116	Yes
Pentachlorobiphenyl	78.1*	9.27	34.8	42.1	69.3	112	131	Yes
Hexachlorobiphenyl	48.7*	8.89	40.2	60.7	53.3	33.7	55.8	No
Heptachlorobiphenyl	80.8*	6.64	51.4	64.4	72.3	102	113	Yes
Octachlorobiphenyl	101	3.33	51.2	97.0	89.4	131	134	Yes
Butyl benzyl phthalate	59.1*	9.53	10.3	75.1	4.01	123	83.8	Yes
O-cymene	18.4*	2.51	27.5	9.54	36.2	9.14	9.50	Yes

Table 5-10. (cont.)

Compound	Estimated Average Recovery (%)	S.E.[2]	Estimated Batch Recoveries (%)[1] 1	2	3	4	5	Sig. Batch Slope Effect?
D-limonene	46.9*	11.9	16.6	53.0	27.5	73.7	63.6	No
Octamethyl-cyclotetrasiloxane	29.5*	3.23	8.28	40.8	50.8	19.1	28.7	Yes

(1) These are estimates of the parameters β_i (i=1,...,5) in the batch slopes model in Table 5-9.

(2) Standard error in the estimated average recovery.

* Significantly different from 100% at the 0.05 level.

Note: Large differences in batch intercepts for p,p-DDE prohibit calculating interpretable batch recoveries.

Table 5-11. Tests for Significant Differences in Batch Slopes Among Selected Batches for Spiked Target Compounds

Compound[1]	Significance Levels		
	Test of Equal Batch Recoveries Among Batches 1-5	Test of Equal Batch Recoveries Among Batches 1-3 Only	Test of Differences in Recoveries between Batches 1-3 and Batches 4-5
Pesticides			
p,p-DDT	0.0003*	0.389	0.0001*
Heptachlor epoxide	0.023*	0.812	0.0018*
Trans-nonachlor	0.101	0.210	0.027*
Dieldrin	0.0018*	0.094	0.071
Chlorobenzenes			
1,4-Dichlorobenzene	0.0067*	0.083	0.0013*
Hexachlorobenzene	0.031*	0.205	0.0059*
PCBs			
Butyl benzyl phthalate	0.0016*	0.016*	0.0005*
O-cymene	0.023*	0.0032*	0.0026*
D-limonene	0.254	0.410	0.066
Octamethyl cyclotetrasiloxane	0.0018*	0.0006*	0.077

(1) p,p-DDE not included in this table (see discussion)

* Significance occurs at the 0.05 level.

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Table 5-12. Predicted Concentrations and Coefficients of Variation at Each Spike Level for Spiked Target Compounds Analyzed by the Batch Slopes Model

Compound	Control		Average Low Spike Level		Average High Spike Level	
	Pred. Conc. (ng/g)	C.V. (%)	Pred. Conc. (ng/g)	C.V. (%)	Pred. Conc. (ng/g)	C.V. (%)
P.P-DDT(*)	204.59	9.2	257.15	7.5	413.82	6.4
Heptachlor epoxide(*)	97.32	22.1	120.67	17.9	190.22	12.4
Trans-nonachlor	223.84	44.4	254.84	42.0	347.25	53.5
Dieldrin (corrected)(*)	65.50	79.1	81.61	69.0	129.66	78.9
1,4-Dichlorobenzene(*)	137.87	71.9	278.94	38.8	699.99	28.6
Hexachlorobenzene(*)	68.59	18.4	118.55	11.2	267.45	7.8
Tetrachlorobiphenyls(*)	84.66	30.8	184.36	14.7	480.51	8.1
Pentachlorobiphenyls(*)	193.54	51.5	273.77	38.0	512.27	30.3
Hexachlorobiphenyls	1015.34	7.6	1080.30	7.3	1273.22	7.7
Heptachlorobiphenyls(*)	693.02	20.6	898.93	16.4	1513.50	13.1
Butyl benzyl phthalate(*)	51.31	69.4	68.31	61.7	119.06	80.9
O-cymene(*)	6.22	186.9	23.50	64.2	75.06	53.4
D-limonene	104.37	45.1	132.68	37.1	217.10	34.4
Octamethyl-cyclo.(*)	2.25	501.4	20.02	81.9	72.97	66.6

All compounds but O-cymene and Octamethyl-cyclotetrasiloxane have predicted control concentrations which are significantly different from zero at the 0.05 level.

(*) Average recoveries only from batches 1-3 used in calculations.

For all but p,p-DDE, the batch slopes model provided a good fit to the surrogate-adjusted data. The estimate of average recovery for p,p-DDE was outside of valid ranges, emphasizing the inappropriateness of estimating batch recoveries for this compound. Batch recoveries were not interpretable for p,p-DDE due to large differences in batch intercepts. Thus no estimated batch recoveries were reported for p,p-DDE in Table 5-10.

For the other compounds, a t-test was performed at the 0.05 significance level to determine if the average recovery was significantly different from 100%. All compounds except p,p-DDE and octachlorobiphenyl had average recoveries significantly greater than 100%. For twelve of the compounds, the average recovery was significantly less than 100%. Five compounds had average recoveries less than 50%: o-cymene (18.4%), octamethyl-cyclotetrasiloxane (29.5%), dieldrin (46.2%), D-limonene (46.9%), and hexachlorobiphenyl (48.7%). Two compounds had average recoveries significantly greater than 100%: hexachlorobenzene (110%) and p,p-DDT (124%).

Estimates of the individual batch recoveries from the batch slopes model are shown in the remaining columns of Table 5-10. Also present are the results of an F-test to determine if significant differences exist among the batch recoveries at the 0.05 significance level. This test determines the presence of batch effects.

Significant differences among the five batch recoveries were observed for twelve compounds. For virtually all of these compounds, the differences seem to arise from the large recoveries in Batches 4 and 5 relative to the first three batches. For p,p-DDT, the estimated recoveries in Batches 4 and 5 average a 65% increase over the first three batches. Similar results are observed for PCBs and other pesticides.

F-tests on linear combinations of the estimated batch recoveries were performed to determine significant differences among these recoveries. The significance levels for the test of equal recoveries among the five batches are listed in Table 5-10

for each spiked target compound except p,p-DDE, where batch recoveries could not be accurately estimated. Because of the apparent difference in estimated batch recoveries between Batches 1-3 and Batches 4-5, Table 5-10 also contains significance levels for testing differences between these two groups of batches, as well as among the first three batches only. For eleven of the fifteen spiked target compounds in Table 5-10, the estimated recoveries in Batches 1-3 differ significantly (at the 0.05 level) from the estimated recoveries in Batches 4-5. However, only three of these compounds have significant differences in estimated recoveries among Batches 1-3 only. Thus the following conclusions can be made from Table 5-10:

- The systematic difference in recoveries between Batches 1-3 and Batches 4-5 appears real,
- There appear to be no additional systematic batch effects beyond that observed in Batches 1-3 versus Batches 4-5.

The first conclusion states that it is not suitable to treat all batch effects as random as was done in the FY87 analysis of dioxins and furans. The presence of a systematic batch effect indicates that some batch correction is necessary when analyzing the composite data. However, any additional batch effects beyond the Batches 1-3 versus Batches 4-5 effect can be treated as random.

For spiked target compounds, Table 5-12 presents the predicted average concentration and estimated coefficient of variation (CV) for each compound and spike level, as derived by the batch slopes model. These results were used to characterize the precision of the analytical method. Except for o-cymene and octamethyl-cyclotetrasiloxane (which had very low recoveries), all predicted concentrations at the zero spike level were significantly greater than zero at the 0.05 significance level.

This is consistent with the fact that the target compounds were detected in nearly all of the QC control samples (Table 5-5).

Whenever the batch slopes model indicated a significant batch effect present, average recoveries from only the first three batches were used to calculate predicted concentrations and CVs for the compound. This reflects the assumption that the primary trend in batch effects is due to Batches 4 and 5 having higher recoveries compared to the first three batches, leading to biases in the results from Batches 4 and 5.

From Table 5-12, the relative precision of measured concentrations tends to be better for pesticides and PCBs compared with other groups of compounds. At the control level, the CVs for pesticides and PCBs range from 7.6% to 51.5%, with a CV of 71.9% for the more volatile 1,4-Dichlorobenzene. The CVs for all of the pesticides and PCBs are below 79% in the spiked samples. Meanwhile, except for D-limonene (whose CVs rival the pesticides and PCBs), the CVs for phthalates and other compounds are above 50% for control and spiked samples.

Because batch recoveries could not be estimated for p,p-DDE (m/z=288 and m/z=316) based on the observed results and spike levels, the batch intercepts model was fit to this compound. The batch intercepts model provides for background levels to be estimated for each batch. Thus batch effects were determined by testing for equality of the batch background levels. Table 5-13 contains the results of fitting the batch intercepts model to p,p-DDE. For both sets of p,p-DDE results, the test for batch effects is highly significant. As apparent in the QC data plots, the estimated background levels for Batches 4 and 5 are over twice the level of the first three batches. This extreme difference in background levels contributes to the inability to estimate batch recoveries. Thus the results of the batch intercepts model fitting for p,p-DDE indicate that differences between the two "batch classes" (Batches 1-3 versus 4-5) are highly significant, as was seen for most of the spiked target compounds.

Table 5-13. Estimated Batch Background Levels and Average Background Level for the Two Methods of Reporting p,p-DDE Concentrations, as Estimated by the Batch Intercepts Model

Compound	Est. Avg. Background Level (ng/g)	S.E.[2]	Estimated Batch Background Level (ng/g)[1]				
			1	2	3	4	5
P,P-DDE (m/z=288)	2872	157	2162	1896	1615	4473	4215
P,P-DDE (m/z=316)	2684	158	2098	1796	1149	4476	3900

(1) These are estimates of the parameters α_i (i=1,...,5) in the batch intercepts model in Table 5-9.

(2) Standard error of the estimated average background level.

5.3.3.2 Unspiked Compounds. Results of statistical analysis of unspiked target compound concentrations in QC samples are presented in Table 5-14. This table presents significance levels for differences between batches and between sample types. Batch effects were significant at the 0.05 level for oxychlordane and Di-n-butyl phthalate. Significant batch effects for oxychlordane are attributed to the large number of not detected readings in Batch 1. A very high percentage of not detected readings for oxychlordane in Batch 1 is also present among the composite samples. Since the frequency of not detected oxychlordane readings substantially decreases after Batch 1, the Batch 1 oxychlordane results tend to be suspect.

None of the unspiked target compounds showed a significant effect due to the sample type. Thus these data can be considered as control sample results for the unspiked compounds. All of these samples are used to determine within-batch measurement error.

Precision was estimated for the unspiked compounds at the control level based on the above analysis of variance model. The precision summary is presented in Table 5-15. The predicted control level reflects all QC samples, as it was determined that no sample type effect existed. Because data exist for all sample types within each batch, the predicted concentration is equal to the average concentration across the 15 QC samples. The standard deviation of the predicted concentration is equal to the mean-squared error estimated by the model.

The precision summary in Table 5-15 indicates that two compounds (Bis (2-ethylhexyl) phthalate and hexyl acetate) have CVs above 100%. These compounds have one extreme observation in at least one batch, at levels up to four times the value of the other results within the batch. Other compounds also show high variability in the data within each batch, especially between not detected results and detected results.

Table 5-14. Results of Statistical Analysis of QC Data on Unspiked Target Compounds

Compound	Significance Level of Batch Effect	Significance Level of Sample Type Effect
Pesticides		
Beta-BHC	0.626	0.643
Oxychlordane	0.009	0.634
PAHs		
Naphthalene	0.545	0.698
Phthalate Esters		
Di-n-butyl phthalate	0.050	0.073
Bis (2-ethylhexyl) phthalate	0.496	0.119
Other (qualitative)		
1-nonene	0.488	0.613
1,2,4-Trimethylbenzene	0.144	0.199
Hexyl acetate	0.771	0.342

Table 5-15. Predicted Concentrations and Coefficients of Variation for Unspiked Target Compounds at the Control Level

Compound	Predicted Control Concentration (ng/g)	Coefficient of Variation (%)
Pesticides		
Beta-BHC	213.4	76.0
Oxychlordane (all batches)	105.9	34.1
Oxychlordane (Batch 1 removed)	129.2	31.8
PAHs		
Naphthalene	9.731	44.9
Phthalate Esters		
Di-N-Butyl phthalate	39.79	47.3
Bis (2-ethylhexyl) phthalate	309.1	126.0
Other (qualitative)		
1-nonene	452.0	73.6
1,2,4-trimethylbenzene	36.00	77.5
Hexyl acetate	120.6	116.1

Note: These statistics reflect results for all QC samples.

Coefficient of variation = $\frac{\text{Square root of mean-squared error}}{\text{Predicted concentration}}$.

5.3.4 Conclusions

The following summarizes the conclusions and findings of the QC data analysis (courses of action formulated from these conclusions are underlined):

1. Significant batch effects appear among the 16 spiked target compound concentrations. The primary batch effect is due to the high recovery and background in Batches 4 and 5 compared to the other three batches. Because this difference between "batch classes" is prevalent in nearly all of the spiked target compounds, it is necessary to include an effect for Batches 4-5 versus Batches 1-3 in the model used to analyze the composite samples. Any other batch effects were assumed to be random and thus were not considered in model adjustments.

2. The difference between "batch classes" was not as significant among the eight unspiked target compounds. However, differences in control level concentrations between batches were noted for oxychlordane and di-n-butyl phthalate. In particular, nearly every QC and composite sample indicated a not-detected result for oxychlordane in Batch 1. As a result, all Batch 1 concentrations for oxychlordane will be deleted prior to composite data analysis.

3. Seven of the target compounds were detected among the five method blanks. All three target phthalates were included among these seven compounds. In particular, bis (2-ethylhexyl) phthalate was detected in all four method blanks which were analyzed for phthalates. D-limonene and octamethyl-cyclotetrasiloxane, also detected in the method blanks, were among those compounds with relatively low recoveries.

4. High background levels relative to the spiking levels were observed for a few spiked target compounds. In particular, the spike levels for p,p-DDE were no more than 10% of the observed background level. For this reason, and because of large differences in background level among the batches, batch recoveries could not be estimated for p,p-DDE. Other compounds with high background levels relative to spiking levels were p,p-DDT, heptachlor epoxide, trans-nonachlor, hexachlorobenzene, and D-limonene.

5. Estimated average recoveries for spiked target compounds were significantly below 100% for all but p,p-DDT and hexachlorobenzene, where they were significantly above 100%. O-cymene, D-limonene,

octamethyl-cyclotetrasiloxane, dieldrin, and hexachlorobiphenyl had average recoveries below 50%. Most estimated batch recoveries for all compounds were less than 100% for Batches 1-3, while many compounds had estimated batch recoveries above 100% for Batches 4 and 5.

6. Characterization of measurement precision for spiked target compounds indicated that better precision was observed for pesticides and PCBs. Precision was worse for phthalates and "other" compounds, with coefficients of variation (CVs) exceeding 50%. For unspiked target compounds, CVs ranged from 32 to 126 percent.

7. Except for o-cymene and octamethyl-cyclotetrasiloxane (which had very low recoveries), all predicted concentrations at the zero spike level were greater than zero at the 0.05 significance level.

8. The relationship between measured and spiked concentrations for spiked target compounds was generally linear over the range of spiked concentrations, but the variability within each batch was high.

The above findings in the QC data were used to reevaluate the status of each target compound prior to composite data analysis. Several compounds had recovery and contamination problems as summarized above. <u>As a result of findings from the statistical analysis on QC data, the following compounds have been removed from the list of target compounds on which statistical analysis of composite data is performed</u>:

<u>Bis (2-ethylhexyl) phthalate</u>

- detected in all method blanks analyzed for this compound.
- low precision results.

<u>Di-n-butyl phthalate</u>

- detected in two of the four analyzed method blanks.
- high levels of not-detected results among the composite samples in Batches 3 and 5 make these batch results suspect.

Butyl benzyl phthalate

- detected in two of the four method blanks analyzed for this compound.
- the low-spiked result in Batch 3 was not detected, although spiked amounts were not below estimated background.

1,2,4-Trimethylbenzene

- detected in the method blank for Batch 3.
- percent detected among composite samples in Batches 4 and 5 is very low compared to the other three batches, making these batch results suspect.

O-cymene

- recoveries extremely low for all spiked QC samples, even though the spiked amounts were above estimated background. All results for spiked sampled failed to meet DQOs.
- percent detected among composite samples in Batch 1 is low compared to the other batches.

D-limonene

- detected in two of the five method blanks.
- recoveries extremely low for spiked QC compounds.

Octamethyl-cyclotetrasiloxane

- detected in the method blank for Batch 3.
- recoveries extremely low for all spiked QC samples, even though the spiked amounts were above estimated background. All results for spiked samples failed to meet DQOs.
- percent detected among composite samples in Batch 1 is low compared to the other batches. The percentage of detected results increased with the batch ID number.

A total of 17 compounds remained classified as target compounds for statistical analysis following analysis of the QC data. However, only limited analyses were performed on the qualitative compounds hexyl acetate and 1-nonene.

6.0 STATISTICAL METHODOLOGY

This section discusses the statistical methodology applied in the FY86 NHATS composite sample data analysis. The statistical analysis of FY86 NHATS data had three objectives:

- Estimate average concentration levels of target semivolatile compounds in the adipose tissue of individuals in the U.S. population as well as in various demographic subpopulations.
- Estimate standard errors and construct confidence intervals for these average levels.
- Perform statistical hypothesis tests to determine if average concentration levels of target semivolatiles in the U.S. population differ significantly by any of four demographic factors (geographic region, age group, race group, and sex group).

The "additive model", a statistical model developed to estimate average concentration levels in individual specimens by analyzing NHATS composite data, was fit to the FY86 data to address each of the above objectives. The additive model involves an iterative weighted generalized least squares method to estimate model parameters representing demographic effects. The resulting parameter estimates are approximately normally distributed for large samples. This approximate normality is used to construct confidence intervals and hypothesis tests. Derivation and validation of the additive model is presented in Orban and Lordo (1989).

Section 6.1 briefly presents the additive model and its necessary modifications in analyzing the FY86 data. The methods used to obtain estimates of average concentrations for target compounds, standard errors for these estimates, and hypothesis tests for the significance of demographic effects on the concentrations are presented in Section 6.2.

6.1 THE ADDITIVE MODEL

In order to expand the NHATS to address a broader range of compounds, it was necessary to develop mass spectrometry-based analytical methods that provided detailed chemical information and supported method specificity. These analytical methods required larger tissue samples than the available samples from individual patients. As a result, the individual adipose tissue specimens were composited prior to chemical analysis. The additive model was developed to achieve the NHATS statistical objectives under the sample compositing scenario.

The additive model was used to analyze the FY87 NHATS dioxin and furan concentrations in composite samples (USEPA, 1991). The FY86 NHATS was the first study in which the additive model was applied to semivolatile composite data. Orban and Lordo (1989) have shown that the additive model has the following attractive features:

- Under very general assumptions, the additive model produces asymptotically unbiased estimates of average concentration levels in the population.
- The additive model establishes a more tractable relationship between the distribution of analyte concentrations in individuals and the distribution of measured concentrations from the composite samples.

The latter feature is particularly important because individual specimens are collected, but the chemical analysis is performed on composite samples.

Table 6-1 lists the categories of the four analysis factors of interest to the NHATS. The additive model assumes that the four analysis factors have fixed additive effects on the average concentrations in specimens. This assumption subdivides the population into 48 "subpopulations" defined by the 4x3x2x2=48 unique combinations of categories for the four factors.

Table 6-1. NHATS Analysis Factors and Categories

Analysis Factor	Category	Number of Categories
Census region	Northeast North Central South West	4
Age group	0-14 years 15-44 years 45+ years	3
Race group	Caucasian Noncaucasian	2
Sex group	Male Female	2
Total Number of Subpopulations (combinations of the four analysis factors):		**48**

In addition to the four analysis factors, there are three ancillary factors that have random effects on NHATS data. Two of these factors have random effects on the actual concentration in individual specimens. They are:

- effect of MSA sampling
- effect of sampling individuals within MSAs (and selecting specimens from individual donors)

The third has a random effect on the measured composite concentrations:

- measurement error of compound concentrations in the composite samples.

A fourth ancillary factor applied specifically to the FY86 composite data is the fixed effect of laboratory batches 4 and 5 on the measured composite concentrations. **Analysis of FY86**

QC sample data (Section 5.3) found significant differences for a majority of target compounds in the measured concentrations for Batches 4 and 5 versus those in the first three batches. Thus a "batch class" factor has been included in the additive model for analysis of FY86 NHATS semivolatile data on composite samples.

From these assumptions, the actual concentration $C_{ijk\ell mn}$ in a specimen from the i^{th} donor in MSA j, census region k, age group ℓ, sex m, and race group n, is represented by

$$C_{ijk\ell mn} = \mu + CR_k + A_\ell + S_m + R_n + MSA_j + \epsilon_{ij} \quad , \qquad (6\text{-}1)$$

where μ is a constant,

CR_k is the fixed effect of census region k (k=1,2,3,4),

A_ℓ is the fixed effect of age group ℓ (ℓ=1,2,3),

S_m is the fixed effect of sex group m (m=1,2),

R_n is the fixed effect of race group n (n=1,2),

MSA_j is the random effect of selecting MSA j (j=1,2,...),

ϵ_{ij} is the random effect of selecting individual i in MSA j .

To uniquely define the fixed effect parameters, let

$$CR_1+CR_2+CR_3+CR_4 = A_1+A_2+A_3 = S_1+S_2 = R_1+R_2 = 0.$$

Thus CR_4, A_3, S_2, and R_2 are defined as a linear combination of other effects, leaving eight fixed parameters in (6-1) which can be uniquely estimated.

The effect MSA_j in (6-1) is a random effect due to the selection of MSAs prior to selecting individual specimens. This effect is assumed to have mean zero and variance σ_m^2. Meanwhile, the effect ϵ_{ij} in (6-1) is random due to selecting individuals randomly within an MSA. The distribution of ϵ_{ij} has mean zero

and variance σ^2_ϵ and is independent from the distribution of MSA_j. Data analysis results through the history of the NHATS program have concluded that variation in specimen concentrations is proportional to the average concentration level. This finding is generally true in most environmental monitoring programs where chemical concentrations are measured. Thus if μ_s is the average concentration level in subpopulation s, then it is assumed that for subpopulation s (s=1,...,48), there exists a positive number b such that:

$$\sigma_\epsilon = b\mu_s \ .$$

For notational simplicity we let

$$\mu_s = \mu + CR_k + A_\ell + S_m + R_n \ ,$$

where the combination of indices k, ℓ, m, and n define subpopulation s.

Equation (6-1) defines the model for the actual concentration in a specimen collected in the FY86 NHATS. However, as specimens are composited prior to chemical analysis, measured specimen concentrations $C_{ijk\ell mn}$ are not observed. Instead, data are obtained from the chemical analysis of <u>composite</u> samples. Assuming data exist for C composites, and letting Y_h represent the measured concentration of composite h (h=1,...,C), the natural additive effects of compositing imply that

$$Y_h = \frac{\sum_s \sum_j \sum_i C_h(i,j,s)\, C_{ijs}}{M_h} + I_h B_{45} + \gamma_h \ , \qquad (6\text{-}2)$$

where C_{ijs} is the actual concentration in specimen i from MSA j and subpopulation s,

$C_h(i,j,s)$ is equal to 1 if specimen i from MSA j and subpopulation s is in composite h, and is equal to

zero otherwise,

M_h is the number of specimens in composite h,

B_{45} is the fixed effect of analysis in Batches 4 and 5 on the composite concentration,

I_h is equal to 1 if composite h was analyzed in Batches 4 or 5, and is equal to zero otherwise, and

γ_h is random measurement error associated with composite h, assumed to have mean zero and variance σ^2_γ.

Because C_{ijs} is associated with demographic effects as specified in equation (6-1), equation (6-2) relates the measured composite concentrations with the demographic effects in Table 6-1. Note that the term B_{45} has been placed in the model in (6-2) as a result of the QC data analysis on FY86 NHATS data. It is not a standard term in the additive model for all NHATS applications.

The statistical analysis performed on the additive model in (6-2) will be explained in terms of matrix notation. Matrices are denoted by capital letters. Matrices and vectors are denoted in bold. Let

$$\boldsymbol{\beta} = (\mu, CR_1, CR_2, CR_3, A_1, A_2, S_1, R_1, B_{45})'$$

be the 9x1 vector of fixed effects from equations (6-1) and (6-2) on the vector of composite concentrations $\mathbf{y} = (Y_1, Y_2, \ldots, Y_C)'$. Fixed effects omitted from $\boldsymbol{\beta}$ can be specified as a linear combination of the effects in $\boldsymbol{\beta}$. Let $\mu = (\mu_1, \ldots, \mu_{48})'$ be a 48x1 vector containing the unknown average concentrations from the 48 subpopulations. Then μ is calculated as $\mu = \mathbf{X}\boldsymbol{\beta}$ for some 48x9 design matrix $\mathbf{X}$.

If the QC data analysis (Section 5.3) found the average concentration in Batches 4-5 to be significantly different from that for the first three batches, the matrix $\mathbf{X}$ is constructed so that μ will depend on the effect B_{45}. In this situation, two average concentrations will be associated with each

subpopulation, one for Batches 4-5 and one for Batches 1-3. This is due to potential biases attributed to the results in Batches 4 and 5.

The expected value of the composite concentrations **y** is given by

$$E(\mathbf{y}) = \mathbf{Z}\mu = \mathbf{ZX}\beta = \mathbf{D}\beta \quad , \qquad (6\text{-}3)$$

where **Z** is a Cx48 composite design matrix. Thus, according to the additive model, both the actual concentrations of the individual specimens and the measured concentrations of the composite samples have expected values that are linear combinations of the additive effects of the fixed analysis factors in β.

Orban and Lordo (1989) also show that the variance-covariance matrix of **y** (denoted by $\mathbf{V}_y$) is a block diagonal matrix that depends on σ^2_m, σ^2_ϵ, and σ^2_γ.

6.2 STATISTICAL ANALYSIS OF COMPOSITE SAMPLES

This section describes the specific methods used to achieve the statistical objectives. The estimation methods are discussed in Section 6.2.1, and the hypothesis testing procedures are presented in Section 6.2.2. This section refers to terms and symbols presented in Section 6.1.

6.2.1 Estimation

6.2.1.1 Estimating Native Compound Levels. The specific quantities estimated for the FY86 NHATS are the average concentrations in the adipose tissue of the U.S. population and the average concentrations for each of the eleven "marginal" demographic populations defined by the categories listed in Table 6-1. These estimates were calculated in three steps:

1. The additive model parameters (vector β in Section 6.1) were estimated using a method called *iterative weighted generalized least squares* (IWGLS).

2. Estimates of average concentration levels in the 48 subpopulations defined by the four analysis factors (vector μ in Section 6.1) were calculated from the parameter estimates.

3. National and marginal population estimates were obtained by taking weighted averages of the appropriate subpopulation estimates in μ. Weights were proportional to the population counts from the 1980 U.S. Census.

To obtain asymptotically unbiased estimates of the fixed effects in β, it is not necessary to make any assumptions about the form of the distributions of the random effects in equation (6-2). If the variance-covariance matrix $\mathbf{V_y}$ of the vector of measured composite sample concentrations $\mathbf{y}$ were known, the method of generalized least squares (GLS) produces estimates of β that are unbiased and have minimum variance among all unbiased estimates. Furthermore, if the errors are normally distributed, the GLS estimates are equivalent to the maximum likelihood estimates. The GLS estimate of β is given by

$$\hat{\beta} = (\mathbf{D}'\mathbf{V_y}^{-1}\mathbf{D})^{-1}\mathbf{D}'\mathbf{V_y}^{-1}\mathbf{y} \quad , \qquad (6\text{-}4)$$

where D is defined in (6-3). The variance-covariance matrix of $\hat{\beta}$ is given by

$$\Sigma_{\beta} = (\mathbf{D}'\mathbf{V_y}^{-1}\mathbf{D})^{-1}$$

Unfortunately, $\mathbf{V_y}$ depends on three unknown variance components (σ^2_m, σ^2_ϵ, and σ^2_γ) from (6-1) and (6-2), as well as on the vector β. Therefore, Orban and Lordo (1989) proposed a method involving iterative weighting. Thus the method is called iterative weighted generalized least squares (IWGLS).

The IWGLS procedure requires starting values for the unknown parameters. These starting values were calculated using

the P3V program of the BMDP™ software package. This program uses a maximum likelihood procedure in fitting a mixed model. The resulting estimate of V_y was then used in the GLS formula to produce a revised estimate of β. The IWGLS procedure provided continual updating of the estimates for V_y, continuing until convergence criteria on the estimate of β and the error sum or squares were met. Orban and Lordo (1989) discuss this method in more detail and describe special computer programs in the SAS® System for implementing IWGLS. They also provide formulas for calculating the standard errors of the estimates.

If $\hat{\beta}$ denotes the final estimate of β from the IWGLS procedure, then an estimate of the average concentration level in each of the 48 subpopulations is calculated by

$$\hat{\mu} = X\hat{\beta} ,$$

where X is a design matrix. The variance-covariance matrix of $\hat{\mu}$ is given by

$$\Sigma_{\mu} = X\Sigma_{\beta}X' = X(D'V_y^{-1}D)^{-1}X' .$$

The estimates in $\hat{\mu}$ are affected whenever batch class effects are present.

Weighted averages of the appropriate subpopulation concentrations $\hat{\mu}_s$ are calculated to estimate "marginal" averages for the categories of each analysis factor. For example, if the set of 12 of the 48 subpopulations found in the Northeast census region is represented by NE, then the estimated average concentration in the Northeast census region is given by

$$M_{NE} = \sum_{s \epsilon NE} w_s \hat{\mu}_s , \qquad (6\text{-}5)$$

where w_s is the proportion of total population in the Northeast census region that is found in subpopulation s (as determined by

1980 U.S. Census figures). Marginal estimates were calculated for four census regions, three age groups, two race groups, and two sex groups. The U.S. population estimate was calculated in the same way, with weights corresponding to the proportion of the U.S. population in each subpopulation.

Standard errors for the marginal estimates were calculated based on the standard errors of the subpopulation estimates $\hat{\mu}_s$. If $\mathrm{Var}(\hat{\mu}_s)$ indicates the estimated variance of $\hat{\mu}_s$, then the standard error of the marginal estimate of $\hat{M}_{NE}$ in (6-5) is given by

$$SE(\hat{M}_{NE}) = \sqrt{\sum_{s \in NE} w_s^2 \mathrm{Var}(\hat{\mu}_s)} \quad , \tag{6-6}$$

where NE and w_s are as defined in (6-5). An approximate 95% confidence interval for each estimate was calculated by adding and subtracting two times the standard error of the estimates.

6.2.1.2 Characterizing PCB Results. Laboratory analysis in the FY86 NHATS measured the concentrations of each of the ten PCB homologs in the composite samples. These concentration estimates were integrated to characterize the nature of PCBs detected in adipose tissue.

If μ_i is the average concentration level (ng/g) of the i^{th} PCB homolog (only μ_4 through μ_8 were estimated in the statistical analysis), then the characterization considered the following three sets of information:

- Total PCB concentration (ng/g) -- the sum of the estimated concentrations for each homolog:

$$total \quad PCB = \sum_{i=1}^{10} \mu_i \tag{6-7}$$

- Chlorobiphenyl distribution across homologs (%) -- the percentage of the total PCB concentration attributed to the i^{th} homolog (i=1,...,10):

$$\text{chlorobiphenyl distribution}_i = \frac{\mu_i}{\text{total PCB}} * 100\% \qquad (6\text{-}8)$$

- Chlorination level (%) -- the sum of the chlorobiphenyl distribution percentages, each weighted by the homolog's chlorine mass fraction (ClMF):

$$\text{level of chlorination} = \sum_{i=1}^{10} ClMF_i * \left(\frac{\mu_i}{\text{total PCB}} * 100\% \right) \qquad (6\text{-}9)$$

These PCB parameters were estimated by substituting estimates of the homolog concentrations μ_i in the above equations, as obtained from the statistical analysis (Section 6.2.1.1). However, statistical analysis was performed only on five of the ten PCB homologs (tetra- through octa-CB). The remaining five homologs were each detected in no more than 30% of the FY86 NHATS composite samples. Thus in estimating the above PCB parameters, it is assumed that μ_i=0 for i=1,2,3,9,10. While this approach may lead to an underestimate of total PCB concentration, the extent of underestimation is expected to be very low. To estimate the level of chlorination, the value of the ClMF is 0.4856 for tetra-CB, 0.5430 for penta-CB, 0.5893 for hexa-CB, 0.6277 for hepta-CB, and 0.6598 for octa-CB.

The standard errors of the above PCB parameters were calculated from the variability estimates in the average concentration levels for the individual PCB homologs (Section 6.2.1.1). If $\hat{\mu_i}$ is the estimate of μ_i as obtained from the statistical analysis, then standard error estimates are given as:

(6-10)

standard error of total PCB:

(6-11)

standard error of chlorobiphenyl distribution percentages:

$$SE_{totPCB} = \sqrt{\sum_{l=4}^{8} SE(\hat{\mu}_l)^2}$$

$$SE_{CDI} = \frac{100}{total\ PCB} * \sqrt{SE(\hat{\mu}_l)^2 + (SE_{totPCB} * \hat{\mu}_l / total\ PCB)^2}$$

standard error of level of chlorination:

$$SE_{loc} = \sqrt{\sum_{l=4}^{8} (CIMF_l * SE_{CDI})^2} \qquad (6\text{-}12)$$

Approximate 95% confidence bounds for the PCB parameters were taken as plus and minus two standard errors.

6.2.2 Hypothesis Testing

Hypothesis tests were performed to determine if average concentration levels differ significantly by any of the geographic or demographic factors. The specific hypotheses tested were

H_{CR}: $CR_1 = CR_2 = CR_3 = CR_4 = 0$,
H_{AGE}: $A_1 = A_2 = A_3 = 0$,
H_{SEX}: $S_1 = S_2 = 0$,
H_{RACE}: $R_1 = R_2 = 0$,
H_{B45}: $B_{45} = 0$.

The hypothesis H_{CR}, for example, states that there are no differences in average concentration levels among the four census regions. Each hypothesis was two-tailed; that is, each alternative was that at least one effect was nonzero and different from the others.

In order to test these hypotheses, it was necessary to make specific distribution assumptions for the random effects. It was assumed that the errors associated with sampling MSAs,

sampling individuals within MSAs, and measuring concentrations were independent and normally distributed. The additive effect of compositing specimens suggests that the normality assumption is reasonable because specimen sampling errors are averaged in the composite sample. Statistical theory states that averages and sums are approximately normally distributed. Distributional assumptions were tested for all target compounds using probability plots and residual analysis.

The likelihood ratio method was used to test the above hypotheses. In this process, the additive model is fit to the observed data both including and excluding the effects to be tested. According to asymptotic theory, the log of the ratio of the likelihood functions from these two fits has approximately a chi-squared distribution, with degrees of freedom equal to the number of independent parameters constrained under the null hypothesis. Orban and Lordo (1989) developed programs in the SAS® System to perform these tests.

7.0 RESULTS

This section contains the results of the statistical analysis of the FY86 NHATS for semivolatiles in human adipose tissue. The applied statistical methods were discussed in Chapter 6. The objectives of the statistical analysis were as follows:

- Estimate average concentration levels of target compounds for individuals in the U.S. population and in various subpopulations;
- Calculate standard errors and confidence bounds on these average levels;
- Perform statistical hypothesis tests to determine if average levels differ significantly between various levels of demographic factors of interest.

Statistical analysis was performed on data obtained from laboratory analysis of 50 composite samples. The composites were prepared using a total of 671 adipose tissue specimens from sampled cadavers and surgical patients. Each composite contained from three to 24 specimens, with an average of 13.4 specimens per composite. The specimens within each sample originated from a common census division and age group but may have differed among sex and race groups. Additional information on sample and composite design is presented in Chapters 2 and 3.

A descriptive summary of the observed concentrations for the 111 semivolatiles is provided in Section 7.1. Statistical analysis was performed only on "target" semivolatiles (identified in Chapter 5) that were detected in a majority of the 50 composite samples and which met specific data quality objectives. Resulting from this statistical analysis, estimates of average subpopulation concentrations are presented in Section 7.2, along with standard errors and confidence bounds on these estimates. Section 7.3 presents the results of statistical hypothesis testing to identify significant effects of demographic factors on average concentration levels. Section 7.4 describes the outlier

detection procedures that identified potential data errors to be corrected prior to conducting the statistical analysis. Finally, as part of the commitment to overall data quality in this program, procedures were implemented to demonstrate the validity of the statistical methodology applied to the FY86 NHATS data. The results of this data validation procedure are presented in Section 7.5.

Unless otherwise specified, all statistical analyses were performed on composite concentrations adjusted for recoveries of surrogate compounds. This adjustment, discussed in Section 5.2, corrected for systematic error identifiable through the surrogate recovery data.

7.1 DESCRIPTIVE STATISTICS

Prior to statistical modelling of target compounds, simple descriptive statistics were generated on the measured concentrations for all 111 semivolatiles analyzed in the NHATS FY86 campaign. These statistics summarized the laboratory results across all 50 FY86 composite samples and consisted of the following:

- arithmetic average;
- standard deviation;
- standard error of the average;
- percent of samples with detected results (duplicated from Table 5-1);
- average level of detection (LOD).

Table 7-1 presents these statistics across the 111 semivolatiles for measured concentrations adjusted for surrogate recoveries, as well as on the unadjusted concentrations.

A compound is detected within a composite sample if the result is classified as either a trace or positive quantifiable reading. Prior to summarizing the data for a given compound, the measured concentrations for all samples with not-detected outcomes were replaced by one-half of the reported LOD. While the LOD itself was not adjusted for surrogate recoveries, the

Table 7-1. Descriptive Statistics of NHATS FY86 Semivolatile Compound Concentrations Based on All 50 Composite Samples[1]

Compound ID Number and Name	Percent Detected	Avg. LOD (ng/g)	Unadjusted Conc.[2] (ng/g) Avg. Conc.	Std. Dev.	Std. Error of Avg.	Adjusted Conc.[3] (ng/g) Avg. Conc.	Std. Dev.	Std. Error of Avg.
PESTICIDES								
1 P,P-DDT	96	9.14	227.	264.	37.	200.	216.	31.
2 O,P-DDT	0	10.9	5.46	4.99	0.71	4.79	4.08	0.58
3 P,P-DDE (M/Z=288)	100		3010.	2570.	360.	2650.	2100.	300.
3 P,P-DDE (M/Z=316)	100		2950.	2990.	420.	2590.	2440.	350.
4 O,P-DDE	0	13.7	6.87	6.29	0.89	6.03	5.13	0.73
5 O,P-DDD	0	13.5	6.75	6.17	0.87	5.93	5.04	0.71
6 ALPHA-BHC	0	11.0	5.50	5.04	0.71	4.83	4.11	0.58
7 BETA-BHC	92	30.8	209.	142.	20.	184.	116.	16.
8 DELTA-BHC	0	12.3	6.15	5.63	0.80	5.40	4.60	0.65
9 GAMMA-BHC(LINDANE)	4	11.7	8.74	17.3	2.45	9.01	16.3	2.30
10 ALDRIN	0	11.6	5.79	5.26	0.74	5.08	4.30	0.61
11 HEPTACHLOR	0	35.2	17.6	84.2	11.9	15.5	68.7	9.7
12 HEPTACHLOR EPOXIDE	94	31.9	81.3	46.5	6.6	63.7	33.1	4.7
13 OXYCHLORDANE	78	20.0	123.	86.	12.	108.	70.	10.
14 TRANS-NONACHLOR	92	26.9	161.	122.	17.	141.	99.	14.
15 GAMMA-CHLORDANE	0	10.8	5.41	4.95	0.70	4.75	4.04	0.57
16 MIREX	32	10.9	12.1	12.2	1.7	10.6	10.0	1.4
60 DIELDRIN	12	123.	70.0	54.6	7.7	61.5	44.6	6.3
60 DIELDRIN (CORRECTED)	62		54.3	58.8	8.3	47.7	48.0	6.8
61 ENDRIN	0	146.	72.8	56.6	8.0	64.0	46.2	6.5
62 ENDRIN KETONE	2	85.3	43.4	33.2	4.7	38.2	27.1	3.8
CHLOROBENZENES								
17 1,3-DICHLOROBENZENE	0	10.1	5.04	4.62	0.65	6.65	5.67	0.80
18 1,4-DICHLOROBENZENE	86	16.7	78.4	75.6	10.7	103.	93.	13.
19 1,2-DICHLOROBENZENE	0	10.3	5.14	4.63	0.66	6.77	5.69	0.80
20 1,2,3-TRICHLOROBENZENE	0	11.8	5.88	5.38	0.76	9.48	7.89	1.12
21 1,2,4-TRICHLOROBENZENE	0	10.2	5.08	4.65	0.66	8.19	6.82	0.96
22 1,3,5-TRICHLOROBENZENE	0	11.1	5.53	5.06	0.72	8.92	7.43	1.05
23 1,2,3,4-TETRACHLOROBENZENE	0	11.7	5.84	5.35	0.76	7.62	6.48	0.92

Table 7-1. (cont.)

Compound ID Number and Name		Percent Detected	Avg. LOD (ng/g)	Unadjusted Conc.[2] (ng/g) Avg. Conc.	Unadjusted Conc.[2] (ng/g) Std. Dev.	Unadjusted Conc.[2] (ng/g) Std. Error of Avg.	Adjusted Conc.[3] (ng/g) Avg. Conc.	Adjusted Conc.[3] (ng/g) Std. Dev.	Adjusted Conc.[3] (ng/g) Std. Error of Avg.
	CHLOROBENZENES (cont.)								
24	1,2,3,5-TETRACHLOROBENZENE	0	11.6	5.79	5.30	0.75	7.56	6.42	0.91
25	1,2,4,5-TETRACHLOROBENZENE	0	10.8	5.38	4.93	0.70	7.02	5.97	0.84
26	PENTACHLOROBENZENE	0	10.1	5.04	4.62	0.65	6.65	5.67	0.80
27	HEXACHLOROBENZENE	98	33.0	54.7	36.5	5.2	55.1	34.6	4.9
	PAHs								
41	NAPHTHALENE	84	13.6	20.5	17.9	2.5	20.3	17.3	2.4
42	ACENAPHTHALENE	0	11.0	5.51	5.04	0.71	5.46	4.87	0.69
43	ACENAPHTHENE	0	10.7	5.36	4.90	0.69	5.31	4.74	0.67
44	FLUORENE	0	12.2	6.09	5.58	0.79	6.04	5.39	0.76
45	PHENANTHRENE	8	11.1	5.92	5.14	0.73	5.87	4.97	0.70
46	FLUORANTHENE	2	10.7	5.44	4.90	0.69	5.39	4.73	0.67
47	PYRENE	0	10.2	5.11	4.68	0.66	5.06	4.52	0.64
48	CHRYSENE	4	10.7	5.61	4.99	0.71	5.56	4.82	0.68
49	BENZO (A) PYRENE	0	9.81	4.91	4.49	0.63	4.86	4.34	0.61
	PCBs								
50	MONOCHLOROBIPHENYLS	0	12.8	6.41	7.42	1.05	6.25	6.84	0.97
51	DICHLOROBIPHENYLS	0	13.0	6.49	7.48	1.06	5.84	6.14	0.87
52	TRICHLOROBIPHENYLS	30	20.2	16.5	14.7	2.1	14.8	12.0	1.7
53	TETRACHLOROBIPHENYLS	66	69.6	88.1	75.8	10.7	70.1	56.1	7.9
54	PENTACHLOROBIPHENYLS	88	65.0	188.	151.	21.	157.	115.	16.
55	HEXACHLOROBIPHENYLS	94	110.	422.	296.	42.	351.	226.	32.
56	HEPTACHLOROBIPHENYLS	86	65.8	176.	188.	27.	146.	143.	20.
57	OCTACHLOROBIPHENYLS	44	33.9	60.7	78.7	11.1	51.9	60.4	8.5
58	NONACHLOROBIPHENYLS	26	32.3	25.7	29.2	4.1	23.1	24.0	3.4
59	DECACHLOROBIPHENYL	28	43.7	32.6	30.3	4.3	31.1	25.0	3.5

Table 7-1. (cont.)

Compound ID Number and Name		Percent Detected	Avg. LOD (ng/g)	Unadjusted Conc.[2] (ng/g) Avg. Conc.	Std. Dev.	Std. Error of Avg.	Adjusted Conc.[3] (ng/g) Avg. Conc.	Std. Dev.	Std. Error of Avg.
	PHTHALATE ESTERS								
63	DIMETHYL PHTHALATE	0	27.1	13.6	10.5	1.5	13.1	9.5	1.3
64	DIETHYL PHTHALATE	10	27.9	17.9	19.1	2.7	17.2	17.2	2.4
65	DI-N-BUTYL PHTHALATE	76	23.6	63.0	117	16.5	60.8	105	14.9
66	BUTYL BENZYL PHTHALATE	72	26.6	58.0	52.4	7.4	55.9	47.2	6.7
67	BIS (2-ETHYLHEXYL) PHTHALATE	78	27.4	1010.	3930.	560.	975.	4E3.	500.
	PHOSPHATE TRIESTERS								
68	TRIBUTYL PHOSPHATE	0	115.	57.7	44.8	6.3	55.6	40.4	5.7
69	TRIS (2-CHLOROETHYL) PHOSPHATE	0	139.	69.4	54.0	7.6	67.0	48.6	6.9
70	TRIS (2,3-DIBROMOPROPYL) PHOSPHATE	0	137.	68.5	53.2	7.5	66.0	48.0	6.8
71	TRIPHENYL PHOSPHATE	4	50.7	30.4	40.3	5.7	29.3	36.3	5.1
72	TRITOLYL PHOSPHATE	2	48.0	24.3	18.6	2.6	23.5	16.8	2.4
	OTHER								
28	BIPHENYL	0	9.68	4.84	4.43	0.63	4.67	3.99	0.56
29	1,2-DIBROMO-3-CHLORO PROPANE	0	11.7	5.83	5.34	0.75	5.62	4.81	0.68
30	HEXACHLORO BUTADIENE	0	12.0	5.98	5.48	0.77	5.76	4.93	0.70
31	HEXACHLORO CYCLOPENTADIENE	0	10.3	5.16	4.73	0.67	4.98	4.26	0.60
32	2,2',4',5-TETRABROMO BIPHENYL	0	12.4	6.22	5.70	0.81	6.00	5.13	0.73
33	O-CYMENE	80	17.7	21.0	14.9	2.1	20.3	13.4	1.9
34	D-LIMONENE	96	11.7	264.	174.	25.	254.	157.	22.
35	D,L-ISOBORNEOL	0	11.3	5.66	5.18	0.73	5.45	4.66	0.66
36	1-INDANONE	0	11.2	5.59	5.12	0.72	5.39	4.61	0.65
37	2-INDANONE	0	10.7	5.34	4.89	0.69	5.15	4.40	0.62
38	BUTYLATED HYDROXYTOLUENE	18	11.3	11.8	24.5	3.5	11.4	22.1	3.1
39	COUMARIN	0	10.7	5.34	4.89	0.69	5.15	4.41	0.62
40	OCTAMETHYL-CYCLOTETRASILOXANE	72	17.8	46.7	56.5	8.0	45.1	50.9	7.2
73	ETHYL HYDROCINNAMATE	2	57.3	29.1	22.2	3.1	28.0	20.0	2.8

Table 7-1. (cont.)

	Compound ID Number and Name	Percent Detected	Avg. LOD (ng/g)	Unadjusted Conc.[2] (ng/g) Avg. Conc.	Unadjusted Conc.[2] (ng/g) Std. Dev.	Unadjusted Conc.[2] (ng/g) Std. Error of Avg.	Adjusted Conc.[3] (ng/g) Avg. Conc.	Adjusted Conc.[3] (ng/g) Std. Dev.	Adjusted Conc.[3] (ng/g) Std. Error of Avg.
	OTHER (cont.)								
74	2-METHOXY-3-METHYLPYRAZINE	0	50.5	25.3	19.6	2.8	24.4	17.7	2.5
75	2,2',4,4',5-PENTACHLORO DIPHENYL ETHER	0	5.97	2.99	2.32	0.33	2.88	2.09	0.30
76	4-CHLORO-P-TERPHENYL	0	40.8	20.4	15.8	2.2	19.7	14.3	2.0
77	TRICHLORO-P-TERPHENYL	0	62.3	31.1	24.2	3.4	30.0	21.8	3.1
78	2-PHENYL PHENOL	24	24.0	93.7	295	41.7	90.4	265	37.5
	PESTICIDES (QUALITATIVE)[4]								
85	ISOPHORONE	16	5.00	5.50	13.9	1.96	4.83	11.3	1.60
86	DICHLOROVOS	2	5.00	3.65	8.13	1.15	3.21	6.64	0.94
98	CHLORPYRIFOS	28	5.00	7.00	9.01	1.27	6.15	7.35	1.04
99	ISOPROPALIN	10	10.0	5.50	1.52	0.21	4.83	1.24	0.17
100	BUTACHLOR	12	5.00	9.60	31.2	4.41	8.44	25.4	3.60
101	NITROFEN	8	5.00	16.1	59.1	8.4	14.1	48.3	6.8
102	PERTHANE	0	10.0	5.00	0.00	0.0	4.39	0.00	0.0
106	DICOFOL	6	5.00	11.2	44.2	6.2	9.80	36.1	5.10
107	P.P'-METHOXYCHLOR	0	10.0	5.00	0.00	0.0	4.39	0.00	0.0
	CHLORINATED AROMATICS (QUALITATIVE)[4]								
88	2,4,6-TRICHLOROANISOLE	0	10.0	5.00	0.00	0.0	4.82	0.00	0.0
89	2,4,6-TRICHLOROPHENOL	0	10.0	5.00	0.00	0.0	4.82	0.00	0.0
90	2,4,5-TRICHLOROPHENOL	0	10.0	5.00	0.00	0.0	4.82	0.00	0.0
91	2,3,6-TRICHLOROANISOLE	0	10.0	5.00	0.00	0.0	4.82	0.00	0.0
92	2,3,6-TRICHLOROPHENOL	0	10.0	5.00	0.00	0.0	4.82	0.00	0.0
95	PENTACHLOROANISOLE	2	10.0	5.10	0.71	0.10	4.92	0.64	0.09
96	PENTACHLORONITROBENZENE	0	5.00	2.50	0.00	0.0	2.41	0.00	0.0
97	2,3,4-TRICHLOROANISOLE	4	10.0	10.0	28.5	4.0	9.64	25.7	3.63
110	OCTACHLORONAPHTHALENE	2	10.0	5.30	2.12	0.30	5.11	1.91	0.27

Table 7-1. (cont.)

Compound ID Number and Name	Percent Detected	Avg. LOD (ng/g)	Unadjusted Conc.[2] (ng/g) Avg. Conc.	Std. Dev.	Std. Error of Avg.	Adjusted Conc.[3] (ng/g) Avg. Conc.	Std. Dev.	Std. Error of Avg.
PAH'S (QUALITATIVE)[4]								
105 BENZO (A) ANTHRACENE	26	5.00	4.45	3.32	0.47	4.29	2.99	0.42
108 BENZO (B) FLUORANTHENE	10	5.00	3.79	4.76	0.67	3.66	4.29	0.61
109 BENZO (K) FLUORANTHENE	4	5.00	8.60	42.1	5.95	8.29	37.9	5.36
111 DIBENZO (A,H) ANTHRACENE	0	5.00	2.50	0.00	0.0	2.41	0.00	0.0
OTHER (QUALITATIVE)[4]								
79 1-NONENE	50	20.0	112.	173.	24.	108.	156.	22.
80 CUMENE	34	5.00	11.9	28.7	4.1	11.4	25.9	3.7
81 1,2,4-TRIMETHYLBENZENE	62	5.00	39.5	43.7	6.2	38.1	39.4	5.6
82 HEXYL ACETATE	82	5.00	132.	166.	23.	128.	149.	21.
83 1,3-DIETHYLBENZENE	8	10.0	6.20	4.11	0.58	5.98	3.70	0.52
84 1,4-DIETHYLBENZENE	0	10.0	5.00	0.00	0.0	4.82	0.00	0.0
87 QUINOLINE	8	10.0	15.6	57.2	8.1	15.0	51.5	7.3
93 DIBENZOFURAN	0	20.0	10.0	0.0	0.0	9.64	0.00	0.0
94 CHLORDANE	2	10.0	6.90	13.4	1.90	6.65	12.1	1.71
103 CHLOROBENZYLATE	0	10.0	5.00	0.00	0.0	4.82	0.00	0.0
104 BIS (2-ETHYLHEXYL) ADIPATE	10	9.89	11.9	22.0	3.1	11.4	19.8	2.8

(1) Descriptive statistics are simple averages, standard deviations, and standard errors of the average using standard statistical formulas. Concentration statistics expressed in ng/g. Concentrations for not detected results are replaced by one-half of the detection limit (LOD) prior to calculating statistics. Data for all 50 composite samples are included in the statistics for all compounds.

(2) Concentrations as reported by the laboratory, without adjustment for surrogate recoveries (Section 5.2).

(3) Concentrations are adjusted for surrogate recoveries (Section 5.2). These adjusted concentrations are used in further statistical analyses for 17 target compounds (Sections 7.2 through 7.3).

(4) Qualitative compounds were only monitored for detection versus non-detection.

modified measured concentration was adjusted. No LOD was reported for detected compounds within a sample. The percentage of samples in each of three qualifier classifications (not detected, trace, and positive quantifiable) was summarized in Table 5-1 of Chapter 5.

Appendix E contains the minimum, median, and maximum reported concentrations across the 50 composite samples for each of the 111 compounds. These statistics are based on concentrations which are unadjusted for surrogate recoveries.

The descriptive statistics in Table 7-1 are based on simple averages of the measured concentrations within the 50 composite samples. As such they only summarize the observed data. They should not be used to estimate concentration levels within the population. Statistical analyses were implemented to obtain population average estimates for seventeen target semivolatiles meeting specific data quality objectives. The results of these analyses are presented in the following sections.

7.2 POPULATION ESTIMATES FROM STATISTICAL MODELLING

The statistical modelling techniques presented in Chapter 6 were used to determine estimates of average concentrations for selected semivolatiles within subpopulations as well as for the entire nation, to obtain estimates of uncertainty inherent in these estimates, and to identify where significant differences in average concentration were present among subpopulations. These techniques centered around the additive model, which was used to estimate average concentration for individuals as a function of several demographic factors. The results from fitting the additive model to the NHATS FY86 composite data are presented in this section.

Not all of the compounds analyzed in the FY86 NHATS analysis provided sufficient composite concentration data to warrant a meaningful statistical analysis. Seventeen of the 111 compounds were identified as containing a sufficient number of

detected samples and whose analytical measurements were deemed accurate in reflecting the true concentration level. Having a sufficient number of composite samples with detected results ensured that only minimal bias was generated by substituting one-half of the detection limit for the measured concentration whenever the compound was not detected by the analytical method. Method performance was determined from analysis of the QC data (Section 5.3), which indicated the presence of batch effects and the extent that anomalous analytical results were reported. The compounds selected for statistical modelling, as well as the criteria used to select them, were identified in Chapter 5.

Fitting the additive model to the NHATS FY86 data for 17 semivolatiles resulted in average concentration estimates for the entire U.S. population, as well as "marginal" estimates for each of the categories defined by the four analysis factors presented in Table 6-1 (census region, age group, race group, and sex group). The formula for calculating marginal estimates was given in equation (6-5) of Section 6.2.1. The estimates are presented in Table 7-2 for the four census regions, Table 7-3 for the three age groups, Table 7-4 for the two race groups, and Table 7-5 for the two sex groups. Table 7-6 presents estimated concentration estimates for the entire nation. The estimates are asymptotically unbiased and were adjusted for the presence of laboratory batch effects (Batches 1-3 versus 4-5) and for population percentages based on the 1980 U.S. Census.

Accompanying the marginal estimates based on the additive model, standard errors and approximate 95% confidence intervals of these estimates are displayed in Tables 7-2 through 7-6. The standard errors were calculated using equation (6-6) of Section 6.2.1 and are used to characterize the statistical uncertainty in the estimated average concentrations. The standard errors are presented in both absolute and relative terms. The confidence intervals represent the marginal estimate, plus and minus approximately two standard errors. The actual

Table 7-2. Estimates of Average Concentrations[1] for Selected Semivolatiles, with Standard Errors and Approximate 95% Confidence Intervals, According to Census Region from NHATS FY86 Composite Samples

Compound	Census Region	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		Pesticides			
p,p-DDT	North Central	136.	23.7	17.5	(87.8, 184.)
	North East	273.	56.6	20.7	(159., 388.)
	South	132.	23.1	17.5	(85.2, 178.)
	West	202.	50.7	25.1	(99.5, 304.)
p,p-DDE[2]	North Central	1820.	307.	16.8	(1202., 2440.)
	North East	2310.	491.	21.3	(1314., 3299.)
	South	2240.	358.	16.0	(1521., 2968.)
	West	3240.	938.	28.9	(1346., 5134.)
Beta-BHC	North Central	151.	42.7	28.2	(65.0, 237.)
	North East	157.	54.6	34.7	(47.2, 268.)
	South	177.	42.8	24.2	(90.4, 263.)
	West	130.	55.2	42.6	(18.2, 241.)
Heptachlor epoxide	North Central	63.5	7.37	11.6	(48.6, 78.3)
	North East	48.4	9.14	18.9	(30.0, 66.9)
	South	70.5	7.34	10.4	(55.6, 85.3)
	West	37.7	9.37	24.8	(18.8, 56.6)
Oxychlordane[3]	North Central	104.	13.0	12.5	(77.8, 131.)
	North East	107.	15.3	14.3	(75.9, 138.)
	South	126.	13.9	11.1	(97.5, 154.)
	West	113.	15.0	13.3	(82.2, 143.)
Trans-nonachlor	North Central	89.2	26.2	29.4	(36.3, 142.)
	North East	156.	33.5	21.5	(88.1, 223.)
	South	154.	26.2	17.0	(102., 207.)
	West	116.	33.8	29.2	(47.4, 184.)

Table 7-2. (cont.)

Compound	Census Region	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		Pesticides (cont.)			
Dieldrin[4]	North Central	57.3	13.6	23.8	(29.8, 84.8)
	North East	42.7	17.4	40.8	(7.54, 77.9)
	South	37.3	13.7	36.6	(9.74, 64.9)
	West	54.8	17.6	32.2	(19.2, 90.4)
		Chlorobenzenes			
1,4-Dichlorobenzene	North Central	98.1	26.1	26.6	(45.4, 151.)
	North East	77.4	33.4	43.1	(9.98, 145.)
	South	126.	26.2	20.8	(72.9, 179.)
	West	35.7	33.7	94.5	(0.0, 104.)
Hexachlorobenzene	North Central	41.2	5.40	13.1	(30.3, 52.1)
	North East	57.6	8.81	15.3	(39.8, 75.4)
	South	41.7	5.50	13.2	(30.6, 52.9)
	West	74.7	13.6	18.2	(47.2, 102.)
		PAHs			
Naphthalene	North Central	12.7	2.49	19.6	(7.68, 17.7)
	North East	18.8	4.47	23.8	(9.74, 27.8)
	South	27.3	4.80	17.6	(17.6, 37.0)
	West	22.1	6.07	27.5	(9.85, 34.4)
		PCBs			
Tetrachlorobiphenyl	North Central	66.2	8.59	13.0	(48.9, 83.6)
	North East	78.8	11.6	14.7	(55.4, 102.)
	South	46.9	7.91	16.9	(30.9, 62.9)
	West	34.0	10.6	31.2	(12.6, 55.4)

Table 7-2. (cont.)

Compound	Census Region	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		PCBs (cont.)			
Pentachlorobiphenyl	North Central	165.	26.2	15.9	(112., 218.)
	North East	202.	33.5	16.6	(134., 269.)
	South	107.	26.3	24.6	(54.0, 160.)
	West	64.2	33.9	52.8	(0.0, 133.)
Hexachlorobiphenyl	North Central	282.	29.8	10.6	(221., 342.)
	North East	430.	47.0	10.9	(335., 525.)
	South	299.	30.1	10.1	(238., 360.)
	West	250.	40.6	16.2	(168., 332.)
Heptachlorobiphenyl	North Central	101.	37.6	37.2	(25.2, 177.)
	North East	213.	48.1	22.6	(116., 310.)
	South	109.	37.7	34.6	(32.8, 185.)
	West	85.5	48.6	56.8	(0.0, 184.)
Octachlorobiphenyl	North Central	33.7	19.9	58.9	(0.0, 73.9)
	North East	75.3	25.4	33.7	(24.1, 127.)
	South	33.4	19.9	59.6	(0.0, 73.6)
	West	33.9	25.7	75.6	(0.0, 85.8)
Total PCBs[5]	North Central	648.	58.8	9.07	(531., 766.)
	North East	998.	80.2	8.03	(838., 1160.)
	South	595.	59.0	9.91	(477., 713.)
	West	468.	77.0	16.5	(314., 622.)
Level of Chlorination[6]	North Central	57.7%	6.17%	10.7	(45.3%, 70.0%)
	North East	58.5%	5.44%	9.32	(47.6%, 69.4%)
	South	58.4%	6.84%	11.7	(44.7%, 72.1%)
	West	58.8%	11.5%	19.5	(35.8%, 81.7%)

Table 7-2. (cont.)

Compound	Census Region	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
Other (qualitative)					
1-Nonene	North Central	92.2	87.5	94.9	(0.0, 269.)
	North East	214.	112.	52.3	(0.0, 440.)
	South	118.	87.7	74.4	(0.0, 295.)
	West	73.9	113.	153	(0.0, 302.)
Hexyl acetate	North Central	80.0	36.9	46.1	(5.45, 154.)
	North East	142.	47.2	33.2	(47.0, 238.)
	South	171.	37.1	21.7	(96.0, 246.)
	West	76.0	47.7	62.8	(0.0, 172.)

(1) Data adjusted for surrogate recoveries (see Section 5.2).
(2) Estimates are based on 1980 U.S. Census figures.
(3) p,p-DDE concentrations use the following response ion: m/z=316.
(4) Data results from Batch 1 not included in calculations.
(5) Corrected (see Section 5.1.2).
(6) The estimate for Total PCBs is the sum of the estimated averages over the five homologs included in this table (i.e., homologs detected in at least 44% of the NHATS FY86 composite samples).
Estimated percent level of chlorination is calculated as follows:

$$\sum_{i=4}^{8} (A_i * B_i) \quad ,$$

where A_i = estimate of the percent of total PCBs for homolog i,
and B_i = mass fraction of chlorine for homolog i.
(Only the five PCB homologs included in the table are considered in calculating level of chlorination.)

Table 7-3. Estimates of Average Concentrations[1] for Selected Semivolatiles, with Standard Errors and Approximate 95% Confidence Intervals, According to Age Group from NHATS FY86 Composite Samples

Compound	Age Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		Pesticides			
p,p-DDT	0-14 years	73.0	26.6	36.4	(19.4, 127.)
	15-44 years	177.	29.2	16.5	(118., 236.)
	45+ years	252.	32.9	13.1	(186., 319.)
p,p-DDE[2]	0-14 years	1710.	380.	22.1	(948., 2481.)
	15-44 years	2150.	360.	16.8	(1420., 2876.)
	45+ years	3080.	412.	13.4	(2247., 3911.)
Beta-BHC	0-14 years	100.	52.4	52.3	(0.0, 206.)
	15-44 years	124.	41.0	33.0	(41.5, 207.)
	45+ years	247.	35.9	14.5	(175., 320.)
Heptachlor epoxide	0-14 years	32.6	7.57	23.2	(17.3, 47.9)
	15-44 years	51.8	6.11	11.8	(39.4, 64.1)
	45+ years	84.7	5.48	6.5	(73.6, 95.7)
Oxychlordane[3]	0-14 years	52.7	16.0	30.5	(19.9, 85.4)
	15-44 years	119.	12.2	10.2	(94.3, 144.)
	45+ years	150.	11.1	7.4	(128., 173.)
Trans-nonachlor	0-14 years	62.5	32.1	51.4	(0.0, 127.)
	15-44 years	115.	25.2	21.8	(64.4, 166.)
	45+ years	203.	22.0	10.8	(158., 247.)
Dieldrin[4]	0-14 years	67.9	16.7	24.6	(34.1, 102.)
	15-44 years	41.9	13.1	31.3	(15.4, 68.4)
	45+ years	39.4	11.5	29.1	(16.2, 62.5)

Table 7-3. (cont.)

Compound	Age Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		Chlorobenzenes			
1,4-Dichlorobenzene	0-14 years	101.	32.1	31.6	(36.7, 166.)
	15-44 years	66.2	25.1	37.9	(15.6, 117.)
	45+ years	120.	21.9	18.2	(76.0, 165.)
Hexachlorobenzene	0-14 years	35.0	6.64	19.0	(21.5, 48.4)
	15-44 years	47.0	5.83	12.4	(35.2, 58.8)
	45+ years	69.8	6.45	9.3	(56.7, 82.8)
		PAHs			
Naphthalene	0-14 years	24.5	5.59	22.9	(13.2, 35.7)
	15-44 years	18.8	3.19	16.9	(12.4, 25.3)
	45+ years	20.7	2.96	14.3	(14.7, 26.6)
		PCBs			
Tetrachlorobiphenyl	0-14 years	19.4	9.00	46.3	(1.27, 37.6)
	15-44 years	41.8	7.41	17.7	(26.9, 56.8)
	45+ years	105.	8.31	7.9	(88.5, 122.)
Pentachlorobiphenyl	0-14 years	75.6	32.2	42.6	(10.5, 141.)
	15-44 years	107.	25.2	23.5	(56.5, 158.)
	45+ years	218.	22.1	10.1	(174., 263.)
Hexachlorobiphenyl	0-14 years	101.	29.2	29.0	(41.8, 160.)
	15-44 years	306.	30.0	9.8	(245., 367.)
	45+ years	481.	32.5	6.8	(415., 546.)
Heptachlorobiphenyl	0-14 years	26.9	46.2	171	(0.0, 120.)
	15-44 years	112.	36.2	32.4	(38.5, 185.)
	45+ years	217.	31.6	14.6	(153., 281.)

Table 7-3. (cont.)

Compound	Age Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		PCBs (cont.)			
Octachlorobiphenyl	0-14 years	20.9	24.4	117	(0.0, 70.2)
	15-44 years	28.8	19.1	66.3	(0.0, 67.4)
	45+ years	79.5	16.7	21.0	(45.7, 113.)
Total PCBs[5]	0-14 years	244.	68.5	28.1	(107., 381.)
	15-44 years	596.	57.1	9.59	(481., 710.)
	45+ years	1100.	53.8	4.89	(993., 1210.)
Level of Chlorination[6]	0-14 years	57.7%	19.2%	33.2	(19.4%, 96.0%)
	15-44 years	58.4%	6.65%	11.4	(45.1%, 71.7%)
	45+ years	58.3%	3.31%	5.67	(51.7%, 64.9%)
		Other (qualitative)			
1-Nonene	0-14 years	111.	107.	97.1	(0.0, 328.)
	15-44 years	162.	84.1	51.9	(0.0, 332.)
	45+ years	75.5	73.5	97.4	(0.0, 224.)
Hexyl acetate	0-14 years	106.	45.3	42.9	(14.1, 197.)
	15-44 years	121.	35.5	29.5	(48.9, 192.)
	45+ years	139.	31.0	22.3	(76.5, 202.)

(1) Data adjusted for surrogate recoveries (see Section 5.2).
(2) Estimates are based on 1980 U.S. Census figures.
(3) p,p-DDE concentrations use the following response ion: m/z=316.
(4) Data results from Batch 1 not included in calculations.
(5) Corrected (see Section 5.1.2).
(6) The estimate for Total PCBs is the sum of the estimated averages over the five homologs included in this table (i.e., homologs detected in in at least 44% of the NHATS FY86 composite samples).
Estimated percent level of chlorination is calculated as given in the footnotes to Table 7-2.

Table 7-4. Estimates of Average Concentrations[1] for Selected Semivolatiles, with Standard Errors and Approximate 95% Confidence Intervals, According to Race Group from NHATS FY86 Composite Samples

Compound	Race Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		Pesticides			
p,p-DDT	White	152.	22.6	14.9	(106., 197.)
	Nonwhite	301.	74.7	24.8	(150., 452.)
p,p-DDE[2]	White	2250.	300.	13.3	(1642., 2852.)
	Nonwhite	2780.	687.	24.7	(1396., 4173.)
Beta-BHC	White	146.	30.0	20.6	(85.2, 206.)
	Nonwhite	212.	68.8	32.4	(73.3, 351.)
Heptachlor epoxide	White	58.8	4.81	8.2	(49.1, 68.5)
	Nonwhite	51.6	9.74	18.9	(32.0, 71.3)
Oxychlordane[3]	White	116.	9.40	8.1	(96.7, 135.)
	Nonwhite	103.	23.2	22.5	(56.0, 151.)
Trans-nonachlor	White	130.	18.4	14.1	(93.2, 167.)
	Nonwhite	131.	42.2	32.3	(45.6, 216.)
Dieldrin[4]	White	45.6	9.57	21.0	(26.3, 64.9)
	Nonwhite	54.1	22.0	40.6	(9.72, 98.5)
		Chlorobenzenes			
1,4-Dichlorobenzene	White	76.6	18.3	23.9	(39.6, 114.)
	Nonwhite	162.	42.1	26.0	(76.7, 247.)
Hexachlorobenzene	White	51.9	4.71	9.1	(42.4, 61.5)
	Nonwhite	48.2	10.5	21.8	(27.0, 69.4)

Table 7-4. (cont.)

Compound	Race Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		PAHs			
Naphthalene	White	19.6	2.64	13.5	(14.3, 24.9)
	Nonwhite	25.9	6.27	24.2	(13.2, 38.6)
		PCBs			
Tetrachlorobiphenyl	White	53.0	5.99	11.3	(40.9, 65.1)
	Nonwhite	73.0	16.0	21.9	(40.7, 105.)
Pentachlorobiphenyl	White	133.	18.4	13.8	(96.0, 170.)
	Nonwhite	141.	42.3	30.0	(55.7, 226.)
Hexachlorobiphenyl	White	289.	22.9	7.9	(243., 335.)
	Nonwhite	435.	65.2	15.0	(304., 567.)
Heptachlorobiphenyl	White	111.	26.4	23.8	(57.5, 164.)
	Nonwhite	195.	60.6	31.1	(72.8, 318.)
Octachlorobiphenyl	White	37.5	13.9	37.2	(9.36, 65.6)
	Nonwhite	68.2	32.0	46.9	(3.56, 133.)
Total PCBs[5]	White	623.	42.3	6.78	(539., 708.)
	Nonwhite	913.	105.	11.5	(703., 1120.)
Level of chlorination[6]	White	58.2%	4.63%	7.97	(48.9%, 67.4%)
	Nonwhite	58.7%	7.86%	13.4	(43.0%, 74.5%)

Table 7-4. (cont.)

Compound	Race Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
Other (qualitative)					
1-Nonene	White	109.	61.4	56.3	(0.0, 233.)
	Nonwhite	196.	141.	72.1	(0.0, 480.)
Hexyl acetate	White	108.	25.9	23.9	(56.0, 161.)
	Nonwhite	195.	59.6	30.5	(74.8, 316.)

(1) Data adjusted for surrogate recoveries (see Section 5.2).
Estimates are based on 1980 U.S. Census figures.
(2) p,p-DDE concentrations use the following response ion: m/z=316.
(3) Data results from Batch 1 not included in calculations.
(4) Corrected (see Section 5.1.2).
(5) The estimate for Total PCBs is the sum of the estimated averages over the five homologs included in this table (i.e., homologs detected in at least 44% of the NHATS FY86 composite samples).
(6) Estimated percent level of chlorination is calculated as given in the footnotes to Table 7-2.

Table 7-5. Estimates of Average Concentrations[1] for Selected Semivolatiles, with Standard Errors and Approximate 95% Confidence Intervals, According to Sex Group from NHATS FY86 Composite Samples

Compound	Sex Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		Pesticides			
p,p-DDT	Male	172.	27.7	16.1	(116., 228.)
	Female	181.	27.6	15.2	(126., 237.)
p,p-DDE[2]	Male	2240.	369.	16.5	(1490., 2983.)
	Female	2430.	358.	14.7	(1710., 3157.)
Beta-BHC	Male	133.	40.2	30.1	(52.3, 215.)
	Female	179.	36.1	20.2	(106., 252.)
Heptachlor epoxide	Male	59.9	5.99	10.0	(47.8, 72.0)
	Female	55.5	5.46	9.8	(44.5, 66.5)
Oxychlordane[3]	Male	122.	11.8	9.7	(97.5, 146.)
	Female	106.	11.1	10.4	(83.7, 129.)
Trans-nonachlor	Male	160.	24.6	15.4	(111., 210.)
	Female	102.	22.1	21.7	(57.3, 147.)
Dieldrin[4]	Male	45.2	12.8	28.4	(19.3, 71.2)
	Female	48.7	11.5	23.7	(25.4, 72.0)
		Chlorobenzenes			
1,4-Dichlorobenzene	Male	108.	24.6	22.8	(58.1, 157.)
	Female	75.0	22.1	29.4	(30.5, 120.)
Hexachlorobenzene	Male	52.3	6.10	11.7	(40.0, 64.6)
	Female	50.4	5.58	11.1	(39.1, 61.6)

Table 7-5. (cont.)

Compound	Sex Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	95% Confidence Interval (ng/g)
		PAHs			
Naphthalene	Male	20.1	3.20	15.9	(13.6, 26.6)
	Female	21.2	3.13	14.8	(14.9, 27.5)
		PCBs			
Tetrachlorobiphenyl	Male	40.7	7.57	18.6	(25.4, 56.0)
	Female	71.2	7.37	10.3	(56.4, 86.1)
Pentachlorobiphenyl	Male	115.	24.7	21.4	(65.6, 165.)
	Female	153.	22.2	14.5	(108., 197.)
Hexachlorobiphenyl	Male	294.	29.5	10.0	(235., 354.)
	Female	332.	27.5	8.3	(276., 387.)
Heptachlorobiphenyl	Male	148.	35.4	24.0	(76.3, 219.)
	Female	104.	31.8	30.7	(39.3, 168.)
Octachlorobiphenyl	Male	52.5	18.7	35.6	(14.8, 90.3)
	Female	33.4	16.8	50.3	(0.0, 67.3)
Total PCBs[5]	Male	651.	56.0	8.61	(539., 763.)
	Female	692.	51.0	7.36	(591., 794.)
Level of chlorination[6]	Male	58.9%	5.89%	10.0	(47.1%, 70.7%)
	Female	57.8%	5.04%	8.73	(43.0%, 74.5%)

Table 7-5. (cont.)

Compound	Race Group	Estimated Average Conc. (ng/g)	Absolute Standard Error of Estimate (ng/g)	Relative Standard Error of Estimate (%)	rd Errors
Other (qualitative)					
1-Nonene	Male	148.	82.4	55.7	
	Female	101.	74.0	73.5	
Hexyl acetate	Male	107.	34.8	32.4	(37.1, 177.)
	Female	138.	31.2	22.7	(74.7, 201.)

(1) Data adjusted for surrogate recoveries (see Section 5.2).
(2) Estimates are based on 1980 U.S. Census figures.
(3) p,p-DDE concentrations use the following response ion: m/z=316.
(4) Data results from Batch 1 not included in calculations.
(5) Corrected (see Section 5.1.2).
(6) The estimate for Total PCBs is the sum of the estimated averages over the five homologs included in this table (i.e., homologs detected in at least 44% of the NHATS FY86 composite samples). Estimated percent level of chlorination is calculated as given in the footnotes to Table 7-2.

Table 7-6. Estimates of Average Concentrations[1] for Selected Semivolatiles, With Standard Errors and Approximate 95% Confidence Intervals, for the Nation from NHATS FY86 Composite Samples

Compound	Estimate of Avg. Conc. (ng/g)	Absolute Standard Error of Est. (ng/g)	Relative Standard Error of Est. (%)	95% Confidence Interval
Pesticides				
p,p-DDT	177.	19.7	11.2	(137., 217.)
p,p-DDE[2]	2340.	270.	11.6	(1792., 2884.)
Beta-BHC	157.	24.9	15.9	(107., 207.)
Heptachlor epoxide	57.6	4.19	7.3	(49.2, 66.1)
Oxychlordane[3]	114.	7.52	6.6	(98.4, 129.)
Trans-nonachlor	130.	15.3	11.7	(99.6, 161.)
Dieldrin[4]	47.0	7.95	16.9	(31.0, 63.1)
Chlorobenzenes				
1,4-Dichlorobenzene	90.9	15.2	16.7	(60.2, 122.)
Hexachlorobenzene	51.3	3.97	7.7	(43.3, 59.3)
PAHs				
Naphthalene	20.7	2.37	11.4	(15.9, 25.4)
PCBs				
Tetrachlorobiphenyl	56.4	4.70	8.3	(46.9, 65.9)
Pentachlorobiphenyl	135.	15.3	11.4	(104., 165.)
Hexachlorobiphenyl	314.	18.4	5.9	(276., 351.)
Heptachlorobiphenyl	125.	21.9	17.5	(80.7, 169.)
Octachlorobiphenyl	42.7	11.6	27.1	(19.3, 66.1)
Total PCBs[5]	672.	34.6	5.2	(603., 742.)
Level of Chlorination[6]	58.3%	3.54	6.1	(51.2, 65.4)
Other (qualitative)				
1-Nonene	124.	51.0	41.3	(20.6, 227.)
Hexyl acetate	123.	21.5	17.5	(79.5, 166.)

Table 7-6. (cont.)

Notes for Table 7-6:

(1) Data adjusted for surrogate recoveries (see Section 5.2). Estimates are based on 1980 U.S. Census figures.

(2) p,p-DDE concentrations use the following response ion: m/z=316.

(3) Data results from Batch 1 not included in calculations.

(4) Corrected (see Section 5.1.2).

(5) The estimate for Total PCBs is the sum of the estimated averages over the five homologs included in this table (i.e., homologs detected in at least 44% of the NHATS FY86 composite samples).

(6) Estimated percent level of chlorination is calculated as follows:

$$\sum_{i=4}^{8} (A_i * B_i) \quad ,$$

where A_i = estimate of the percent of total PCBs for homolog i,
and B_i = mass fraction of chlorine for homolog i.
(Only the five PCB homologs included in the table are considered in calculating level of chlorination.)

number of standard errors in the confidence interval is determined by the Student-t distribution.

The 17 target compounds for statistical analysis included five PCB homologs (tetra- through octa-chlorobiphenyl). Using the average estimates for these five homologs, estimates of total PCBs and level of chlorination were calculated based on the approach documented in Section 6.2.1.2. The estimates of these two PCB parameters are also included in Tables 7-2 through 7-6. In addition, the chlorobiphenyl distribution across the five PCB homologs, corresponding to the percentage of the total PCB concentration represented within each homolog, is presented in Table 7-7. This table illustrates that the penta-, hexa-, and hepta-chlorobiphenyls represent over 80% of the national average PCB concentration across the five homologs, with hexachlorobiphenyl representing 47% of the total. As will be seen in Chapter 8, similar distributions were observed in previous NHATS campaigns.

Appendix F contains plots of the estimated average concentrations and their associated 95% confidence intervals for the 17 target compounds, as documented in Tables 7-2 through 7-6. One plot exists for each compound and contains statistics for each of the four analysis factors and the entire nation. These plots illustrate the trends observed in the average concentrations across the subpopulations and the variability associated with these trends. Considerable overlapping of the confidence intervals indicate that while average concentrations may differ between subpopulations, they may not differ statistically. The chlorobiphenyl distributions presented in Table 7-7 are also plotted in Appendix F.

Estimates of the average concentrations in the population categories defined by the four demographic factors are presented in Tables 7-2 through 7-6 even if the effects of those factors were not found to be statistically significant through hypothesis testing. For example, regional estimates of average concentration for Beta-BHC range from 151 ng/g in the North

Table 7-7. Chlorobiphenyl Distribution Across the Five Target PCB Homologs in the FY86 NHATS

Demographic Group	Percentage of Total Concentration Across the Five Homologs				
	Tetra-	Penta-	Hexa-	Hepta-	Octa-
North Central	10.2%	25.5%	43.4%	15.6%	5.2%
North East	7.9%	20.2%	43.1%	21.3%	7.5%
South	7.9%	18.0%	50.2%	18.3%	5.6%
West	7.3%	13.7%	53.5%	18.3%	7.3%
0-14 years	8.0%	31.0%	41.3%	11.1%	8.6%
15-44 years	7.0%	18.0%	51.4%	18.7%	4.8%
45+ years	9.6%	19.8%	43.7%	19.7%	7.2%
White	8.5%	21.4%	46.3%	17.8%	6.0%
Nonwhite	8.0%	15.5%	47.7%	21.4%	7.5%
Male	6.3%	17.7%	45.2%	22.7%	8.1%
Female	10.3%	22.0%	47.9%	14.9%	4.8%
Nation	8.4%	20.0%	46.6%	18.6%	6.3%

Note: Homologs not represented in this table were detected in no more than 30% of the NHATS FY86 composite samples. The omitted homologs were not included in calculating total PCBs, and thus the percentages in a given row add to 100%.

Central census region to 177 ng/g in the South census region. However, as further documented in Section 7.3, this difference was not found to be statistically significant.

Table 7-6 indicates that the standard errors of the national estimates among the 17 semivolatiles ranged from 5.9 to 41.3 percent of the estimates. The highest relative standard error was observed with 1-Nonene, which is a qualitative semivolatile compound. Among the four analysis factors, higher relative standard errors were generally noted among subfactors associated with fewer composites, such as the West census region, the 0-14 year age group, and the non-Caucasian race group.

The estimated concentrations for most of the 17 semivolatile compounds appear to increase with age group according to Table 7-3. This result has been observed in data analyses on other NHATS datasets (e.g., FY82 and FY87). Similar trends consistent across the analyzed compounds are not as apparent among census regions, race groups, and sex groups. Statistical conclusions on these effects are based on the hypothesis tests in the next section.

7.3 HYPOTHESIS TESTING

Statistical hypothesis tests were conducted for each of the 17 semivolatile compounds included in the statistical analysis to determine if there are statistically significant differences in average concentrations between individuals from different geographic regions, age groups, race groups, and sex groups. The tests were based on likelihood ratio tests using the additive model analysis and were described in Section 6.2.2.

Table 7-8 lists the attained significance levels for the tests associated with the four analysis factors. In addition, a test was performed to note significance of the effect that being in Batches 4 and 5 has on the measured concentration; this factor was significant among the QC sample data. The attained significance level is the smallest level at which the test can result in rejection of the hypothesis that no differences are

Table 7-8. Significance Levels from Hypothesis Tests for Differences Between Demographic Groups for NHATS FY86 Semivolatiles[1]

Compound	Effects due to ...			
	Census Region[3]	Age Group[3]	Sex Group[4]	Race Group[4]
1-Nonene	0.782	0.751	0.764	0.695
Hexyl acetate	0.301	0.826	0.672	0.445

(1) Data adjusted for surrogate recoveries (see Section 5.2).
(2) Likelihood ratio tests based on the $\chi^2_{(3)}$ distribution.
(3) Likelihood ratio tests based on the $\chi^2_{(2)}$ distribution.
(4) Likelihood ratio tests based on the $\chi^2_{(1)}$ distribution.
(5) p,p-DDE concentrations use the following response ion: m/z=316.
(6) Data results from Batch 1 not included.
(7) Corrected (see Section 5.1.2).

* Significant at the 0.05 level.
** Significant at the 0.01 level.

present between the population averages. For example, the differences among estimated averages of Beta-BHC in the four census regions could only be considered significant at the 0.947 (94.7%) level of significance, while the differences in age group average is significant at the 0.015 (1.5%) level. A significance level of less than 0.05 (5%) is generally required to declare statistical significance.

An apparent conclusion from Table 7-8 is the presence of significantly different estimated average concentrations among the age groups for pesticides, hexachlorobenzene, and PCBs. From Table 7-3, the older age group (45+ years) had the highest estimated average concentration for these compounds, and the youngest age group (0-14 years) had the lowest estimate. The disparity between the older age group and the others is more apparent for the PCBs.

Statistical significance was also observed among census regions for three pesticides, hexachlorobenzene, naphthalene, and three PCB congeners. Levels of p,p-DDT and hexachlorobenzene were highest in the West census region, while for some PCB congeners, levels were lowest in the West census region. However, a consistent trend across the compounds was not observed with census region as was observed with age groups.

The difference in estimated average concentration between caucasian and non-caucasian and between male and female donors were not statistically significant for any of the modelled compounds. The effect of Batches 1-3 versus 4-5 on the measured concentrations in composite samples was also not significant for any of the compounds.

7.4 OUTLIER DETECTION

Prior to conducting the statistical analysis of the FY86 NHATS data, outlier detection procedures were performed to identify possible data entry errors and errors associated with the analytical method. The outlier detection process was performed in multiple stages by Westat, Battelle, and EPA. MRI

reviewed all findings of this process, identified a list of changes to data values resulting from their review, and notified the NHATS project team of these changes. Battelle corrected the database according to MRI's review prior to performing the final statistical analysis.

Westat performed statistical outlier analysis on the following types of data:

- measured concentrations of native analytes,
- internal quantitation standard recoveries,
- LODs, and
- percent lipid values for composite and QC samples.

The methods and findings of these analyses are presented in Rogers (1991). The procedure consisted of three approaches: logic checks, formal outlier identification procedures, and informal outlier identification procedures.

Logic checks were performed prior to database completion, to identify obvious data inconsistencies or coding errors. For example, by printing records with inconsistent entries, the logic check procedure would reveal records having recorded concentrations but a data qualifier of "not detected".

The formal approach to outlier identification in Rogers (1991) assumed that the concentrations and recovery data followed a lognormal distribution, and the percent lipid data followed a normal distribution. A mathematical model was fit to the data, and the extreme studentized deviate (ESD) test was applied to the residuals of the model. This test considered the ratio of the maximum residual to the standard deviation of the residuals. Outliers were identified if this ratio exceeded the appropriate critical value given the significance level (1% or 5%). The form of the simple linear regression models varied among the different types of data (see Table 2 in Rogers (1991)).

Once formal outlier identification procedures were completed, informal identification procedures noted any

additional data which may be in question. These procedures included normality tests on residuals for individual compounds, multivariate tests across multiple compounds (identifying data points which do not conform with a multivariate normal distribution), boxplots to compare measurements of different types, and special outlier comparison tests for the LODs.

In addition to the approach documented in Rogers (1991) to identify outliers among native compound concentrations in composite samples, Battelle identified additional potential outliers by fitting the additive model (Chapter 6) to the preliminary FY86 semivolatile data. Residuals exceeding two standard deviations from zero were reported.

To illustrate patterns due to analysis order and batch, time series plots of the FY86 data were produced. Any outliers and questionable data points were highlighted in these plots. These data plots and listings of statistical outliers were delivered to EPA and to MRI for review.

A total of 50 data points were identified as outliers from the procedures in Rogers (1991). These data points included 24 quantitative concentrations, 6 qualitative concentrations, and 20 recoveries. Of these points, eight were changed as a result of review by MRI. The findings of the outlier analysis identified unusually low surrogate recoveries for two samples, implying that the reported concentrations were suspect for these samples. The outlier report also noted that recoveries in Batch 1 were lower than in later batches, apparently due to changes in lab procedures. These findings supported the need to consider effects of batch in statistical analyses and to correct data for surrogate recoveries.

Forty-four additional data points were identified as potential statistical outliers as a result of fitting the additive model to target compound data. Review of these data by MRI resulted in changes to 16 of the data points.

Battelle made all data corrections to the master database before proceeding with the statistical analysis.

However, as a result of the data review, some of the data points identified in the outlier detection procedure either did not require modification or remained influential after modification. Thus these data points contributed to increased error in fitting the additive model and to inflated variability in parameter estimation and hypothesis testing. The most influential data points are documented in the following section.

7.5 MODEL VALIDATION

As part of the commitment to overall data quality, three types of analyses were performed to evaluate the adequacy of the additive model for use on the FY86 NHATS semivolatile data on the seventeen target compounds. All three analyses were based on comparisons of the observed (i.e., measured) and predicted concentrations for the composite samples. Predicted concentrations were calculated using the IWGLS method applied to the additive model (Chapter 6). Residuals, which were also used in the model validation analysis, were calculated by taking the differences between the observed and predicted concentrations.

Model validation analyses included:

- residual plots,
- normal probability plots, and
- R-squared analysis.

The use of Shapiro-Wilk tests for normality was also considered. However, in this application, the Shapiro-Wilk test was not appropriate because the data were correlated and variances increased with increasing concentrations.

In several of the target compounds, the residual plots (residuals versus predicted concentration) confirmed the model assumption that the variance of the measured concentrations increases with the average concentration. In addition, these plots showed that the distribution of residuals tended to be symmetric about zero across all predicted concentrations. For some compounds, the extent to which residuals were symmetric about zero was less evident at low concentrations, where

predicted levels tended to be larger than the observed level. This finding indicates that the relationship between measured concentration and the model predictors may not be as linear in low concentration ranges relative to larger concentration ranges. Also, the low concentration range can include a substantial number of measured concentrations at or below the detection limit. For compounds whose non-detect percentage approached 50% (such as octachlorobiphenyl, 1-nonene, dieldrin, and tetrachlorobiphenyl), the predicted concentrations in areas close to the detection limit may be more biased in portraying the true concentration than predicted concentrations in higher detectable ranges.

The presence of unusually high or low data points also contributed to an overall lack of fit of the model to the observed data. The data points observed to be among the most "influential" to the model fitting are presented in Table 7-9. The result of fitting the model while including the influential data points is either an underestimate or overestimate by the fitted model in certain concentration ranges.

Normal probability plots for most target compounds resembled a linear pattern, supporting the normality assumption for the errors. However, the linearity assumption for some compounds did not hold in areas of extremely large or small concentrations. This is explained by the larger variances associated with these concentrations, and by the presence of influential data points with large positive or negative residuals.

Table 7-10 lists the R-squared correlations between the observed and predicted concentrations calculated for each target compound. R-squared can be interpreted as the percent of the total variability in the observed concentrations that can be explained by the additive model. The correlations range from 12% (naphthalene) to 65% (tetrachlorobiphenyl). The qualitative compounds have low R-squared values, indicating that their categorical concentrations are not highly correlated with

Table 7-9. Measured Concentrations with High Influence on Determining the Additive Model Fit

Sample ID	Lab. ID	Measured Conc.[1] (ng/g)	Predicted Conc. (ng/g)
p,p-DDT			
ACS8600270	17922	1214	886
Oxychlordane[2]			
ACS8600065	17942	39.2	148.7
ACS8600163	17946	306	139
Trans-nonachlor			
ACS8600163	17946	510	264
Hexachlorobenzene			
ACS8600314	17986	123	67.5
ACS8600207	17968	176	81.1
ACS8600350	17948	192	96.5
Naphthalene			
ACS8600332	17965	66.9	23.5
ACS8600225	17939	99.0	24.6
ACS8600421	17924	70.5	26.3
Tetrachlorobiphenyl			
ACS8600127	17959	249	124
ACS8600092	17909	217	146
Hexachlorobiphenyl			
ACS8600092	17909	1123	493
Heptachlorobiphenyl			
ACS8600289	17919	888	376
Octachlorobiphenyl			
ACS8600289	17919	322	142

Table 7-9. (cont.)

Sample ID	Lab. ID	Measured Conc.[1] (ng/g)	Predicted Conc. (ng/g)
1-Nonene			
ACS8600181	17960	728	261
Hexyl acetate			
ACS8600458	17938	459	45.8
ACS8600252	17926	369	74.2
ACS8600430	17921	729	233
p,p-DDE[3]			
ACS8600163	17946	10716	4062
ACS8600341	17958	11859	5599
Dieldrin[4]			
ACS8600458	17925	212	58.8
ACS8600225	17939	278	194

(1) Data adjusted for surrogate recoveries (see Section 5.2).
(2) Batch 1 results not included in statistical analysis.
(3) p,p-DDE concentrations use the following response ion: m/z=316.
(4) Corrected (see Section 5.1.2).

Table 7-10. R-Squared Correlation Between Observed Concentrations and Concentrations Predicted by the Additive Model for NHATS FY86 Semivolatiles[1]

Compound	R-squared (%)
Pesticides	
p,p-DDT	31
p,p-DDE	49
Beta-BHC	43
Heptachlor epoxide	55
Oxychlordane	43
Trans-nonachlor	55
Dieldrin	13
Chlorobenzenes	
1,4-Dichlorobenzene	29
[illegible]chlorobenzene	46
PAHs	
Naphtha[illegible]	12
PCBs	
Hexachlorobiphenyl	61
Heptachlorobiphenyl	47
Octachlorobiphenyl	37
1-Nonene	23
Hexyl acetate	14

[1] R-squared is the square of the Pearson correlation coefficient. It represents the percent of variability in the data that is explained by the additive model. Data adjusted for surrogate recoveries (see Section 5.2).

predicted values. Note that these R-squared values are not as high as seen with dioxins and furans in the FY87 NHATS (USEPA, 1991). This does not necessarily imply, however, that the additive model is an inadequate fit to the semivolatile compound data. Instead, low R-squared values may indicate that the estimated model effects are small relative to the random error observed in the measured concentrations. The random error is increased by the presence of influential observations such as those in Table 7-9.

8.0 COMPARISON WITH RESULTS FROM PREVIOUS SURVEYS IN THE NHATS PROGRAM

The FY86 NHATS is one of three surveys in the NHATS program to use HRGC/MS analytical methods in measuring the prevalence and levels of semivolatile organic compounds in composited adipose tissue samples. Prior to the FY86 survey, the FY82 and FY84 surveys also performed analysis of semivolatiles on composite samples using HRGC/MS methods. The NHATS FY86 sampling and data analysis approach was designed to allow valid statistical comparisons to be made between the FY86 results and the results from these two surveys.

The NHATS FY82 Broadscan Analysis Study (Mack and Panebianco, 1986) was the first NHATS campaign to employ the HRGC/MS method in characterizing an expanded chemicals list. The objective of the FY82 NHATS was to identify and characterize additional compounds that persist in human adipose tissue but could not be measured with less selective analytical techniques. The FY84 NHATS was designed to establish the comparability of the HRGC/MS and PGC/ECD analytical methods (Westat, 1990). The FY84 NHATS revealed that issues in method comparability were not totally resolved for many of the target semivolatile compounds. This chapter presents comparison of the FY86 NHATS results with the results from the NHATS FY82 and FY84 semivolatile analyses.

There are several differences in the designs and analytical procedures used in these three surveys. These differences are documented in Section 8.1. Only the semivolatile compounds analyzed in the FY86 NHATS and in at least one of the FY82 and FY84 NHATS are included in comparisons. For each of these compounds within each survey, Section 8.2 presents average limits of detection (LODs) and the percentages of detected results among the samples. Statistical procedures were used to compare these detection percentages across surveys. Section 8.3 presents two approaches to calculating descriptive statistics in summarizing measured concentration data within each of the three

surveys at the national level. Finally, statistical comparisons were performed on only those compounds detected in at least 50% of the composite samples within each survey. Section 8.4 presents results of fitting the additive model to these compounds within each survey.

8.1 COMPARISON OF DESIGN AND ANALYTICAL PROCEDURES

8.1.1 Comparison of Study Designs

Similar sampling designs were used for collecting tissue specimens in the FY82, FY84, and FY86 NHATS. A discussion of the FY86 sampling design is found in Chapter 2 of this report. The primary difference in sampling designs between these three surveys is the method of stratification. Prior to the FY85 NHATS, MSAs were selected from strata defined by the nine U.S. Census divisions. Beginning with the FY85 NHATS, sampling strata were redefined to be the seventeen geographic areas that resulted from the intersection of the Census divisions and the ten EPA regions (Table 2-2).

A controlled selection technique (Mack et. al., 1984) was used to maximize the probability of retaining MSAs from one survey design to another. Table 8-1 displays the number of specimens and composites associated with each MSA for each survey. Except for double-collection MSAs, no MSA contributed more than the quota of 27 specimens to the FY86 NHATS design. This was not true for the FY82 and FY84 surveys, where as many as 72 specimens originated from a single-collection MSA. Only five MSAs sampled in the FY82 and FY84 NHATS were not represented in the FY86 NHATS, while only four MSAs were sampled in the FY86 NHATS but not in the other two surveys. It is expected that differences in MSA sampling across the three surveys contribute to only minor differences in concentration estimates.

For each census region, age group, sex group, and race group, Tables 8-2 and 8-3 present summaries of the number of specimens and composites, respectively, originating within these

Table 8-1. Number of Specimens and Composites Within the FY82, FY84, and FY86 NHATS According to MSA

MSA (code and location)		Number of Specimens			Number of Composites[1]		
		FY82	FY84	FY86	FY82	FY84	FY86
800	AKRON, OH	0	6	18	0	1	5
5200	ATLANTA, GA	0	0	27	0	0	8
10000	BIRMINGHAM, AL	40	27	0	5	4	0
11200	BOSTON, MA	0	0	25	0	0	4
16000	CHICAGO, IL	17	37	45	8	6	6
16800	CLEVELAND, OH	44	40	27	8	6	6
18400	COLUMBUS, OH	0	0	14	0	0	3
19200	DALLAS-FORT WORTH, TX	38	26	27	4	4	3
19600	DAVENPORT-ROCK ISLAND-MOLINE, IA-IL	12	9	0	5	2	0
20000	DAYTON, OH	24	24	9	7	6	3
20800	DENVER-BOULDER, CO	10	10	10	2	3	3
21600	DETROIT, MI	9	15	54	3	2	4
23350	ELMIRA, NY	0	17	27	0	4	5
31600	GREENVILLE-SPARTANBURG, SC	14	39	27	9	10	7
42800	LEXINGTON-FAYETTE, KY	45	38	27	5	4	4
44800	LOS ANGELES-LONG BEACH, CA	0	8	4	0	2	2
46000	LUBBOCK, TX	35	12	0	4	4	0
47200	MADISON, WI	40	29	27	8	6	4
49200	MEMPHIS, TN-AR-MS	0	0	23	0	0	4
50000	MIAMI, FL	26	16	27	9	8	8
56000	NEW YORK, NY-NJ	76	0	25	6	0	5
57200	NORFOLK-VA BEACH-PORTSMOUTH, VA-NC	72	43	27	10	9	8
59200	OMAHA, NE-IA	19	60	27	4	5	5
59600	ORLANDO, FL	43	33	0	9	8	0
61600	PHILADELPHIA, PA-NJ	5	7	7	2	1	4
62800	PITTSBURGH, PA	28	25	21	4	4	4
64400	PORTLAND, OR-WA	27	15	16	3	4	3
68200	ROCHESTER, MN	41	29	27	4	4	5
69200	SACRAMENTO, CA	4	0	2	1	0	2
71600	SALT LAKE CITY-OGDEN, UT	19	22	24	3	3	4
72400	SAN ANTONIO, TX	0	27	0	0	4	0
73600	SAN FRANCISCO-OAKLAND, CA	0	0	27	0	0	5
78400	SPOKANE, WA	0	15	12	0	3	3
80000	SPRINGFIELD-CHICOPEE-HOLYOKE, MA-CT	56	37	18	3	4	4
82800	TAMPA-ST PETERSBURG, FL	0	7	8	0	4	3
88400	WASHINGTON, DC-MD-VA	19	16	12	8	6	5
	Totals:	763	689	671	46	46	50

[1] Column entries indicate the number of composites having at least one specimen from the given MSA. The total at the bottom of each column indicates the total number of analyzed composites in the survey. Since specimens within a composite can originate from more than one MSA, this total is not equal to the sum of the column entries.

Table 8-2. Total Number of Specimens Included in Composite Samples Analyzed in the FY82, FY84, and FY86 NHATS, by Subpopulation and Across the Entire Study

Subpopulation	Number of Specimens (% of Total) FY82	FY84	FY86	1980 Census %
Census Region				
Northeast	166 (22%)	86 (12%)	123 (18%)	26%
North Central	206 (27%)	249 (36%)	248 (37%)	22%
South	331 (43%)	284 (41%)	205 (31%)	33%
West	60 (8%)	70 (10%)	95 (14%)	19%
Age Group				
0-14 years	178 (23%)	142 (21%)	108 (16%)	23%
15-44 years	312 (41%)	266 (39%)	221 (33%)	46%
45+ years	273 (36%)	281 (41%)	342 (51%)	31%
Sex				
Male	412 (54%)	352 (51%)	315 (47%)	49%
Female	351 (46%)	337 (49%)	356 (53%)	51%
Race				
White	632 (83%)	579 (84%)	526 (78%)	83%
Nonwhite	131 (17%)	110 (16%)	145 (22%)	17%
Total # of Specimens	763	689	671	

Table 8-3. Total Number of Composite Samples Analyzed in the FY82, FY84, and FY86 NHATS, by Subpopulation and Across the Entire Survey

Subpopulation	Number of Composites (% of Total) FY82	FY84	FY86	1980 Census %
Census Region[1]				
Northeast	9 (20%)	8 (17%)	9 (18%)	26%
North Central	12 (26%)	13 (28%)	16 (32%)	22%
South	19 (41%)	18 (39%)	15 (30%)	33%
West	6 (13%)	7 (15%)	10 (20%)	19%
Age Group[1]				
0-14 years	12 (26%)	10 (22%)	10 (20%)	23%
15-44 years	17 (37%)	19 (41%)	16 (32%)	46%
45+ years	17 (37%)	17 (37%)	24 (48%)	31%
Sex[2]				
Mixed[3]	35	29	18	
Male only	6 (55%)	8 (47%)	14 (44%)	49%
Female only	5 (45%)	9 (53%)	18 (56%)	51%
Race[2]				
Mixed[3]	29	25	29	
White only	11 (65%)	16 (76%)	16 (76%)	83%
Nonwhite only	6 (35%)	5 (24%)	5 (24%)	17%
Total # of Composites	46	46	50	

[1] All specimens within a given composite originated from the same census region and age group.

[2] The percentages for sex and race groups are calculated as the total number of pure composites within each study design. For example, 6 of the 11 (55%) pure sex composites in the FY82 study design were composed of specimens from males only.

[3] Composites containing specimens from both sex (or race) groups.

groups. The distributions of specimens among the geographic and demographic groups were relatively similar across the three surveys. The FY86 survey had higher percentages of specimens from the West census region and the nonwhite race group: two groups in which specimens are generally less procurable than other groups.

The FY82, FY84, and FY86 NHATS also had comparable composite designs (Table 8-3). One of the design criteria for compositing FY84 and FY86 specimens was to maintain similarity to the FY82 design (see Section 3.1). However, the FY86 design stipulated more pure sex composites (i.e., all male or all female) than the FY82 and FY84 designs in order to more accurately estimate differences in concentrations among the sexes. Sixty-four percent of the FY86 composites were pure sex composites, compared to less than forty percent of the composites in the FY82 and FY84 surveys. Overall, the percentages of composites within each population group were similar across the three surveys and with the 1980 Census percentages.

8.1.2 Comparison of Analytical Procedures

To interpret differences in estimated concentrations between the three surveys, it is necessary to consider differences in their analytical methods. While some major differences do exist, the methods were otherwise similar between the three surveys.

One analytical factor having a large potential effect on data comparability between the three surveys is the type and number of internal quantitation standards (IQS) and how these standards are assigned to semivolatile compounds. Native compound concentrations were quantified relative to the IQS findings. Only one IQS was used to quantify the semivolatiles in FY82: anthracene-d_{10}. The FY84 and FY86 surveys included three IQS for quantification of semivolatiles: anthracene-d_{10}, benzo(a)anthracene-d_{12}, and naphthalene-d_8. In addition to

differences caused by the number and type of IQS assigned to each survey, the method of assigning an IQS to each semivolatile differed between the FY84 and FY86 NHATS. Table 8-4 lists those semivolatiles analyzed in both FY84 and FY86 for which the same IQS was assigned in both surveys. Table 8-5 lists the semivolatiles with differing IQS between FY84 and FY86. Differing IQS assignments between surveys must be considered when interpreting differences observed in results from one survey to another.

Average concentration estimates in the FY86 NHATS were based on measured concentrations adjusted for surrogate recoveries (Chapter 7). The adjusted concentrations are more likely to resemble actual concentrations in the sample than unadjusted measured concentrations. Thus for comparison purposes, it was necessary to obtain average concentration estimates in the FY82 and FY84 surveys based on surrogate-adjusted concentrations. Like the IQS, surrogate compounds were matched to specific semivolatile compounds within each survey (Table 5-2) for adjustment purposes. However, the types of surrogate compounds included in each survey also differed. Thus in conducting the comparison, it is noted when surrogate compounds differed among the surveys.

Another issue to consider is that the FY82 and FY86 analyses were conducted at Midwest Research Institute, while the FY84 analysis was performed at Colorado State University. Thus interlaboratory variation is also introduced when comparing FY84 results with the other two surveys.

Other than the differences noted above, the techniques in the analytical methods for semivolatile analyses were essentially equivalent between the three surveys. The flow diagram in Figure 4-1 (Chapter 4) illustrates the order of activities in each campaign. Each procedure required fortification with IQS and surrogate compounds, extraction, removal of bulk lipid, separation, cleanup, and quantification. Extraction was achieved with methylene chloride using a Tekmar

Table 8-4. Semivolatile Compounds Quantitated Using the Same Internal Quantitation Standards (IQS) in NHATS FY84 and FY86.

IQS: Benzo(a)anthracene-d_{12}
p,p-DDT
o,p-DDT
p,p-DDE
o,p-DDD
TRANS-NONACHLOR
MIREX
CHRYSENE
HEXACHLOROBIPHENYL
HEPTACHLOROBIPHENYL
OCTACHLOROBIPHENYL
NONACHLOROBIPHENYL
DECACHLOROBIPHENYL
IQS: Anthracene-d_{10}
ALPHA-BHC
BETA-BHC
DELTA-BHC
GAMMA-BHC(LINDANE)
ALDRIN
HEPTACHLOR
HEPTACHLOR EPOXIDE
OXYCHLORDANE
GAMMA-CHLORDANE
PENTACHLOROBENZENE
HEXACHLOROBENZENE
ACENAPHTHALENE
FLUORENE
PHENANTHRENE
FLUORANTHENE
MONOCHLOROBIPHENYL
DICHLOROBIPHENYL
TRICHLOROBIPHENYL
TETRACHLOROBIPHENYL
IQS: Naphthalene-d_8
1,2,3-TRICHLOROBENZENE
1,2,4-TRICHLOROBENZENE
1,3,5-TRICHLOROBENZENE
NAPHTHALENE

Note: Anthracene-d_{10} was the only IQS used in the FY82 NHATS.

Table 8-5. Semivolatile Compounds Quantitated Using Different Internal Quantitation Standards (IQS) in NHATS FY84 and FY86.

Compound	IQS[1]	
	FY84	FY86
o,p-DDE	B	A
1,2,3,4-TETRACHLOROBENZENE	N	A
1,2,3,5-TETRACHLOROBENZENE	N	A
1,2,4,5-TETRACHLOROBENZENE	N	A
ACENAPHTHENE	N	A
PYRENE	B	A
PENTACHLOROBIPHENYL	B	A

(1) Legend: A = Anthracene-d_{10}
B = Benzo(a)anthracene-d_{12}
N = Naphthalene-d_8

Note: Anthracene-d_{10} was the only IQS used in the FY82 NHATS.

Tissuemizer to promote thorough extraction of lipids. Extracts were filtered through anhydrous sodium sulfate. Gel permeation chromatography was applied to separate target analytes from lipid material. Interference separation was achieved through Florisil column fraction procedures.

8.2. LODs AND PERCENT DETECTION SUMMARIES

A total of 54 quantitative semivolatile compounds were analyzed in the FY86 NHATS and also analyzed in one or both of the FY82 and FY84 NHATS. These compounds form the basis of the descriptive and statistical comparisons in measured concentrations of target compounds across the three surveys. This subsection summarizes the LODs and the percentages of detected results for these compounds in the FY82, FY84, and FY86 NHATS.

An LOD was reported for a compound whenever a trace or not-detected reading was reported for the sample. These LODs (ng/g lipid weight) are averaged and presented in Table 8-6 for the 54 semivolatile compounds. The LODs were not adjusted for surrogate recoveries prior to averaging. Table 8-6 also documents the percent of composite samples with detected readings within each survey for the 54 compounds. Only compounds with at least 50% detected readings within each of the three surveys were considered for further statistical comparisons.

For most compounds, the percentage of samples with detected results was consistent across the surveys. Low detection percentages were reported for most chlorobenzenes (with the exception of hexachlorobenzene), phosphate triesters, and PAHs, while some pesticides (such as p,p-DDE and beta-BHC) had very high detection percentages.

To identify those compounds in Table 8-6 where significant differences were present (at the 0.05 level) in the percent detected value between the three surveys, a chi-square test for homogeneity was used. Among pesticides, significant differences in the percent detected value were present for p,p-

Table 8-6. Average Lipid-Adjusted Limit of Detection (LOD, ng/g) and Percent of Composites with Detected Concentrations, for Compounds Analyzed in the FY86 NHATS and Also Analyzed in the FY82 and/or FY84 NHATS[1]

Compound	FY82		FY84		FY86	
	Mean LOD	(% det.)	Mean LOD	(% det.)	Mean LOD	(% det.)
PESTICIDES						
p,p-DDT*	31.2	(67.6%)	48.7	(88.9%)	9.14	(96.0%)
o,p-DDT			13.5	(0.0%)	10.9	(0.0%)
p,p-DDE	13.7	(100.0%)	352.	(95.5%)		(100.0%)[2]
o,p-DDE			13.2	(4.3%)	13.7	(0.0%)
o,p-DDD			125.	(0.0%)	13.5	(0.0%)
ALPHA-BHC			19.9	(0.0%)	11.0	(0.0%)
BETA-BHC	34.0	(93.0%)	212.	(89.1%)	30.8	(92.0%)
GAMMA-BHC(LINDANE)			18.5	(2.2%)	11.7	(4.0%)
DELTA-BHC			18.2	(0.0%)	12.3	(0.0%)
ALDRIN			13.1	(0.0%)	11.6	(0.0%)
DIELDRIN*	117.	(32.6%)	19.4	(38.5%)	123.	(12.0%)
ENDRIN						(62.0%)[3]
TRANS-NONACHLOR*	45.8	(57.1%)	38.7	(0.0%)	146.	(0.0%)
OXYCHLORDANE			14.2	(95.6%)	26.9	(92.0%)
HEPTACHLOR EPOXIDE*	21.4	(69.8%)	16.5	(82.6%)	20.0	(78.0%)
HEPTACHLOR			15.2	(80.4%)	31.9	(94.0%)
MIREX*	22.6	(14.0%)	19.1	(0.0%)	35.2	(0.0%)
GAMMA-CHLORDANE			13.1	(4.3%)	10.9	(32.0%)
			13.0	(0.0%)	10.8	(0.0%)
CHLOROBENZENES						
1,2-DICHLOROBENZENE*	26.3	(11.6%)			10.3	(0.0%)
1,2,3-TRICHLOROBENZENE			13.0	(0.0%)	11.8	(0.0%)
1,2,4-TRICHLOROBENZENE	25.4	(4.4%)	13.1	(4.3%)	10.2	(0.0%)
1,3,5-TRICHLOROBENZENE			13.0	(0.0%)	11.1	(0.0%)
1,2,3,4-TETRACHLOROBENZENE			13.0	(0.0%)	11.7	(0.0%)
1,2,3,5-TETRACHLOROBENZENE			13.0	(0.0%)	11.6	(0.0%)
1,2,4,5-TETRACHLOROBENZENE			13.0	(0.0%)	10.8	(0.0%)
PENTACHLOROBENZENE	25.9	(0.0%)	13.0	(0.0%)	10.1	(0.0%)
HEXACHLOROBENZENE*	18.5	(79.1%)	15.2	(82.6%)	33.0	(98.0%)

Table 8-6. (cont.)

Compound	FY82 Mean LOD	FY82 (% det.)	FY84 Mean LOD	FY84 (% det.)	FY86 Mean LOD	FY86 (% det.)
PHTHALATE ESTERS						
DIMETHYL PHTHALATE			14.2	(0.0%)	27.1	(0.0%)
DIETHYL PHTHALATE*	47.7	(47.6%)	14.3	(7.7%)	27.9	(10.0%)
DI-N-BUTYL PHTHALATE*	299.	(50.0%)		(100.0%)	23.6	(76.0%)
BUTYL BENZYL PHTHALATE	240.	(73.8%)	24.0	(61.5%)	26.6	(72.0%)
BIS (2-ETHYLHEXYL) PHTHALATE*			38.7	(0.0%)	27.4	(78.0%)
PHOSPHATE TRIESTERS						
TRIBUTYL PHOSPHATE	108.	(2.3%)	14.2	(0.0%)	115.	(0.0%)
TRIPHENYL PHOSPHATE*	333.	(38.1%)	13.5	(61.5%)	50.7	(4.0%)
TRIS (2-CHLOROETHYL) PHOSPHATE	89.7	(2.2%)	38.7	(0.0%)	139.	(0.0%)
TRITOLYL PHOSPHATE			48.7	(0.0%)	48.0	(2.0%)
PAHs						
NAPHTHALENE*	19.3	(41.9%)	13.1	(23.9%)	13.6	(84.0%)
PHENANTHRENE	21.6	(14.0%)	13.0	(21.7%)	11.1	(8.0%)
FLUORANTHENE			14.1	(2.2%)	10.7	(2.0%)
CHRYSENE			16.4	(4.3%)	10.7	(4.0%)
ACENAPHTHENE			13.0	(0.0%)	10.7	(0.0%)
ACENAPHTHALENE			13.1	(0.0%)	11.0	(0.0%)
FLUORENE			14.0	(2.2%)	12.2	(0.0%)
PYRENE	22.6	(0.0%)	12.9	(4.3%)	10.2	(0.0%)
PCBs						
MONOCHLOROBIPHENYL			13.0	(0.0%)	12.8	(0.0%)
DICHLOROBIPHENYL			13.0	(0.0%)	13.0	(0.0%)
TRICHLOROBIPHENYL	20.3	(22.7%)	14.2	(39.1%)	20.2	(30.0%)
TETRACHLOROBIPHENYL	17.8	(54.5%)	31.5	(41.3%)	69.6	(66.0%)
PENTACHLOROBIPHENYL	42.6	(72.7%)	16.4	(84.8%)	65.0	(88.0%)
HEXACHLOROBIPHENYL*	48.4	(75.0%)	13.1	(97.8%)	110.	(94.0%)
HEPTACHLOROBIPHENYL*	50.6	(52.3%)	15.0	(84.4%)	65.8	(86.0%)

Table 8-6. (cont.)

Compound	FY82 Mean LOD	FY82 (% det.)	FY84 Mean LOD	FY84 (% det.)	FY86 Mean LOD	FY86 (% det.)
			PCBs (cont.)			
OCTACHLOROBIPHENYL*	48.8	(40.9%)	13.2	(17.8%)	33.9	(44.0%)
NONACHLOROBIPHENYL	42.3	(13.6%)	19.1	(22.2%)	32.3	(26.0%)
DECACHLOROBIPHENYL*	104.	(6.8%)	20.7	(35.6%)	43.7	(28.0%)

* Percent detection differs signficantly across surveys at the 0.05 level, based on a chi-square test of homogeneity.

(1) LODs were obtained in each survey only for composites having not-detected or trace results. LODs were not adjusted for surrogate recoveries. Statistics are presented only for those compounds analyzed within a given survey.

(2) The detection percentage was 100% under both quantitation ions used in FY86 (see Section 5.1.2).

(3) Detection percentage based on redefined quantitation methods in FY86 (see Section 5.1.2).

DDT, dieldrin, trans-nonachlor, heptachlor epoxide, and mirex. For each of these pesticides, significance was primarily the result of low detection percentages observed in the FY82 survey. For p,p-DDT, the detection percentage increased from 67.6% in FY82 to 96% in FY86. This increase may be partially explained by a substantial reduction in the average LOD for p,p-DDT in the FY86 survey. Percent detection also increased in FY86 for mirex, from below 15% in both FY82 and FY84 to 32% in FY86, while accompanied by a gradual reduction in the average LOD across these surveys.

Percent detection of hexachlorobenzene increased across the FY82 to FY86 surveys, from 79.1% to 98%. These differences across surveys were statistically significant, but were not accompanied by corresponding reductions in the average LOD. The average percent detection declined in FY86 to 4% for triphenyl phosphate from above 38% in the other two surveys; this decline was statistically significant. Naphthalene was the only PAH with a high percent detection in FY86 (84%), leading to statistically significant differences in the percentages across surveys.

Significant differences in percent detection were also observed for diethyl phthalate (where the average percentage dropped substantially from the FY82 value of 47.6%), di-n-butyl phthalate (where the average percentage increased from 50% in FY82 to 100% in FY84), and bis (2-ethylhexyl) phthalate (0% in FY84 to 78% in FY86). However for di-ethyl phthalate, the decreasing percentages were accompanied by decreases in the average LOD. This indicates that overall measured concentrations have decreased across the surveys for this compound, despite potential contaminations in the phthalates for the FY86 survey as ggested by the QC data analysis. The contamination issue was evident for bis (2-ethylhexyl) phthalate, which was detected method blanks in the FY86 analysis.

Significant differences in percent detection across e also observed in the higher-order PCB homologs.

Average percent detection was low in FY82 compared to the other two surveys for hexa-, hepta-, and deca-chlorobiphenyls, leading to statistically significant differences in percent detection across the surveys. However, a corresponding reduction in the average LOD from FY82 to FY84 did not hold for FY86. In fact, the average detection limit in FY86 for these homologs exceeded that for FY82 in hexa- and hepta-chlorobiphenyls. This result appears to agree with other findings indicating unusually high concentrations for these homologs in FY86, which may derive from analytical sources rather than environmental sources.

Thus while average percent detection in FY86 remained at levels consistent with earlier surveys, occasional increases were observed for some compounds. However, the differences in analytical methods and recoveries observed from one survey to another imply that the differences may be the result of analytical rather than environmental effects.

8.3 DESCRIPTIVE STATISTICS ON MEASURED CONCENTRATIONS

A total of 54 semivolatile organic compounds were analyzed in the FY86 NHATS and in at least one of the FY82 and FY84 NHATS. The extent to which statistical comparison of measured concentrations was appropriate among these 54 compounds was determined by initially summarizing the analytical results within each survey through simple descriptive statistics. Some basic differences in the results across surveys were apparent when reviewing summary statistics. The summaries also assisted in interpreting comparison findings.

Initially, scatterplots were produced for each of these compounds in order to identify any large differences or patternistic behavior in the measured concentrations between and within the three surveys. Then, two approaches to calculating descriptive statistics were applied to the concentrations. In the first approach, simple arithmetic averages and standard errors of the measured concentrations were calculated. While these statistics summarize the measured concentrations across

analytical samples, they are not necessarily good estimates of the national average concentration. A better approximation of national average concentration can result by taking weighted averages of the observed concentrations. Thus the second approach was to partition the nation into subpopulations, calculate average concentrations within each subpopulation, and weight each average by the 1980 Census population percentage for its respective subpopulation. The second approach can lead to a improved estimate of national average concentration for each compound, regardless of whether further statistical analysis was warranted on the compound concentrations.

In the descriptive summaries from both approaches, measured concentrations were defined as the total mass detected, divided by the sample lipid weight. Whenever a compound was not detected within a sample, measured concentrations were taken to be one-half of the LOD (as was done in the statistical analyses). The percent detected values in Table 8-6 indicate the frequency with which not-detected results were observed within each compound. The descriptive statistics presented in the following subsections were calculated on measured concentration both adjusted and unadjusted for surrogate recoveries.

8.3.1. Scatterplots of the Sample Concentrations

Prior to calculating descriptive statistics, scatterplots of measured concentrations were generated for all compounds detected in at least 50% of the FY86 samples and which were analyzed in the FY82 NHATS and/or the FY84 NHATS. The scatterplots illustrate any general differences or trends in the concentrations between surveys and between batches within surveys. Plots were generated for concentrations both unadjusted and adjusted for surrogate recoveries. These plots are located in Appendices G and H, respectively.

The concentrations are plotted as a function of the analysis date in these scatterplots. Therefore any trends in the concentrations over time or batches are highlighted in these

plots. In addition, the plotting symbols indicate the age group represented by the result (1 = 0-14 years, 2 = 15-44 years, 3 = 45+ years). Results in Chapter 7 indicated that age group had a significant effect on the values of the measured concentrations.

These plots illustrate the large extent to which increasing concentrations were associated with increasing age for most compounds. Also, the unadjusted concentrations for the FY86 NHATS appeared to be more variable than in the previous surveys, excluding the effects of occasional outliers. This is especially apparent in plots of PCBs and some pesticides. However, variability appears to be more consistent across surveys when considering surrogate-adjusted concentrations. The plots suggest that this is the result of an increase in variability associated with the surrogate-adjusted concentrations across all surveys.

These scatterplots also illustrate apparent trends from batch to batch within a survey. For example, unadjusted concentrations of beta-BHC tend to decrease in later batches in the FY84 analysis. The difference between Batch 1 and the other batches in FY86 oxychlordane concentrations is also evident (recall that Batch 1 data were excluded from statistical analysis for oxychlordane).

The primary purpose of reviewing scatterplots prior to further statistical summaries or analyses was to depict any obvious differences in results across surveys. Extreme differences in the values of the concentrations between surveys would indicate that statistical techniques may not be necessary in making such conclusions. Extreme differences from one survey to another were not apparent for these compounds based on the scatterplots.

8.3.2. Unweighted National Averages

Appendix I presents simple arithmetic averages (with their standard errors) of the measured concentrations among the 54 compounds for each of the three surveys. The averages were

calculated across all composite samples in Table 8-3 where measured concentrations were reported for the given compound. Averages were calculated for two endpoints: on measured concentrations adjusted for surrogate recoveries (Table I-1), and on unadjusted concentrations (i.e., the recorded concentrations) (Table I-2). The adjustment for surrogate recoveries was performed to more accurately estimate actual concentrations within each sample. The adjustment was described in Section 5.2.

With some exceptions, concentrations or LODs were reported for all composites for a given compound analyzed within a survey. However in the FY84 survey, results for dieldrin, endrin, the phthalate esters, and the phosphate triesters were reported in only 13 of the 46 composite samples.

The descriptive statistics in Appendix I were calculated only to summarize the results of the three surveys. Because these summaries ignore demographic effects which were determined to be significantly associated with measured concentration, the descriptive statistics do not necessarily estimate national average concentrations in the respective surveys. Such estimates were obtained from statistical modelling techniques for a limited number of compounds.

8.3.3. Weighted National Averages

Estimates of the national average concentration estimates were obtained in this study through statistical modelling procedures rather than from simple descriptive statistics as discussed above. However, statistical modelling was reserved only for those compounds with sufficiently high detection percentages within each survey. Thus an approach was necessary for calculating more accurate national estimates than the simple descriptive statistics, regardless of detection percentages. To do this, averages of composite concentrations were calculated within each of the three age groups (0-14 years, 15-44 years, 45+ years) and were weighted by the population proportions within each group. Age group was selected for the

weighting criterion because its effect on measured concentrations was most commonly significant across the demographic groups within each survey. In addition, sufficient numbers of sample results existed to provide sufficient accuracy in averages within each age group.

Calculating the weighted national averages was a multistage process. First, unweighted arithmetic averages were calculated for each of the three age groups. Then each age-group average was multiplied by the population proportion in that age group (based on the 1980 Census). These three results were then summed to obtain the final estimate.

Tables 8-7 and 8-8 present the weighted national averages for the 54 compounds analyzed in the FY86 and in the FY82 and/or FY84 NHATS. The results in Table 8-7 are based on the actual measured concentrations, while the results in Table 8-8 are calculated from concentrations adjusted for surrogate recoveries.

Results from these two tables indicate that for some compounds, the values of descriptive statistics differ greatly between surveys. Some of these differences may be more likely due to differences in laboratory methods and instrumentation than to differences rooted in environmental effects. For example, the LODs for some of the phthalate esters and phosphate triesters were found to average much higher in the FY82 NHATS than in the other surveys (Table 8-6), leading to higher average measured concentrations among the FY82 composites for these compounds. The largest difference in average concentration occurred with triphenyl phosphate, where the FY82 weighted average was two orders of magnitude higher than in the other two surveys. Most FY82 composite samples report high concentrations for this compound relative to the other surveys.

The weighted average concentration for bis (2-ethylhexyl) phthalate also increased nearly two orders of magnitude from FY84 to FY86, primarily due to the presence of samples with detected results in FY86 (78%, versus no detected

Table 8-7. Weighted National Averages of Unadjusted Concentrations (ng/g) and Standard Errors for Compounds Analyzed in the FY86 NHATS and Also Analyzed in the FY82 and/or FY84 NHATS[1]

Compound[2]	FY82 Weighted Avg.	FY82 (S.E.)	FY84 Weighted Avg.	FY84 (S.E.)	FY86 Weighted Avg.	FY86 (S.E.)
PESTICIDES						
p,p-DDT	118.	(27.)	88.1	(12.2)	205.	(42.)
o,p-DDT			6.73	(0.24)	5.61	(0.75)
p,p-DDE	1070.	(160.)	796.	(66.)	2530.	(280.)
o,p-DDE			7.19	(0.51)	7.07	(0.94)
o,p-DDD			65.0	(16.7)	6.95	(0.92)
ALPHA-BHC			10.2	(3.6)	5.66	(0.75)
BETA-BHC	176.	(24.)	130.	(17.)	183.	(16.)
GAMMA-BHC(LINDANE)			9.61	(2.67)	9.99	(3.42)
DELTA-BHC			9.26	(1.92)	6.33	(0.84)
ALDRIN			6.58	(0.17)	5.98	(0.80)
DIELDRIN	105.	(23.)	22.2	(6.8)	55.2	(10.0)
ENDRIN			18.1	(3.7)	71.6	(9.0)
TRANS-NONACHLOR	85.0	(22.0)	72.3	(4.8)	142.	(12.)
OXYCHLORDANE			45.7	(3.9)	112.	(10.)
HEPTACHLOR EPOXIDE	48.9	(11.2)	47.1	(4.6)	73.6	(4.6)
HEPTACHLOR			9.56	(1.55)	13.6	(7.7)
MIREX	9.91	(1.45)	7.35	(0.62)	12.5	(1.8)
GAMMA-CHLORDANE			6.55	(0.17)	5.56	(0.74)
CHLOROBENZENES						
1,2-DICHLOROBENZENE	9.67	(1.48)			5.30	(0.68)
1,2,3-TRICHLOROBENZENE			6.55	(0.17)	6.05	(0.81)
1,2,4-TRICHLOROBENZENE	7.01	(0.54)	7.29	(0.54)	5.23	(0.70)
1,3,5-TRICHLOROBENZENE			6.55	(0.17)	5.69	(0.76)
1,2,3,4-TETRACHLOROBENZENE			6.55	(0.17)	6.01	(0.80)
1,2,3,5-TETRACHLOROBENZENE			6.55	(0.17)	5.96	(0.79)
1,2,4,5-TETRACHLOROBENZENE			6.55	(0.17)	5.54	(0.74)
PENTACHLOROBENZENE	6.46	(0.29)	6.55	(0.17)	5.19	(0.69)
HEXACHLOROBENZENE	80.6	(39.9)	23.3	(2.8)	49.3	(3.8)

Table 8-7. (cont.)

Compound[2]	FY82 Weighted Avg.	FY82 (S.E.)	FY84 Weighted Avg.	FY84 (S.E.)	FY86 Weighted Avg.	FY86 (S.E.)
PHTHALATE ESTERS						
DIMETHYL PHTHALATE			7.22	(0.64)	13.3	(1.7)
DIETHYL PHTHALATE	75.2	(25.4)	8.04	(0.85)	17.6	(2.5)
DI-N-BUTYL PHTHALATE	351.	(123.)	202.	(44.)	59.9	(11.6)
BUTYL BENZYL PHTHALATE	237.	(56.)	62.6	(21.3)	62.8	(8.1)
BIS (2-ETHYLHEXYL) PHTHALATE			18.1	(3.7)	869.	(396.)
PHOSPHATE TRIESTERS						
TRIBUTYL PHOSPHATE	32.9	(2.1)	7.22	(0.64)	56.7	(7.1)
TRIPHENYL PHOSPHATE	1630.	(1520.)	57.0	(39.1)	30.9	(6.3)
TRIS (2-CHLOROETHYL) PHOSPHATE	28.9	(3.6)	18.1	(3.7)	68.3	(8.5)
TRITOLYL PHOSPHATE			23.3	(3.7)	24.1	(3.0)
PAHs						
NAPHTHALENE	14.2	(2.1)	9.67	(0.94)	20.1	(2.4)
PHENANTHRENE	8.24	(0.76)	21.3	(7.7)	6.14	(0.76)
FLUORANTHENE			7.25	(0.44)	5.63	(0.74)
CHRYSENE			10.3	(1.7)	5.73	(0.71)
ACENAPHTHENE			6.55	(0.17)	5.52	(0.73)
ACENAPHTHALENE			6.60	(0.18)	5.67	(0.76)
FLUORENE			8.42	(1.41)	6.27	(0.84)
PYRENE	6.50	(0.30)	20.8	(12.1)	5.26	(0.70)
PCBs						
MONOCHLOROBIPHENYL			6.55	(0.17)	6.62	(1.16)
DICHLOROBIPHENYL			6.55	(0.17)	6.70	(1.17)
TRICHLOROBIPHENYL	8.86	(0.73)	10.4	(0.6)	14.2	(1.8)
TETRACHLOROBIPHENYL	20.9	(2.5)	32.5	(3.9)	72.2	(6.3)
PENTACHLOROBIPHENYL	68.2	(9.2)	74.3	(8.7)	162.	(15.)
HEXACHLOROBIPHENYL	122.	(18.)	132.	(11.)	373.	(25.)

Table 8-7. (cont.)

Compound[2]	FY82 Weighted Avg.	FY82 (S.E.)	FY84 Weighted Avg.	FY84 (S.E.)	FY86 Weighted Avg.	FY86 (S.E.)
PCBs (cont.)						
HEPTACHLOROBIPHENYL	59.6	(9.5)	90.6	(11.2)	149.	(17.)
OCTACHLOROBIPHENYL	41.7	(8.8)	12.3	(2.6)	49.0	(7.6)
NONACHLOROBIPHENYL	21.0	(5.5)	13.8	(1.9)	22.7	(3.4)
DECACHLOROBIPHENYL	37.4	(3.3)	15.7	(1.9)	28.2	(3.7)

(1) Weighted averages are the sum of the arithmetic averages of the unadjusted concentrations within each of the three age groups (0-14 years, 15-44 years, 45+ years), each multiplied by the proportion of the national population in that age group according to the 1980 Census (0.23, 0.46, and 0.31, respectively). Statistics are presented only for those compounds analyzed within a given survey.

(2) Concentrations of p,p-DDE and dieldrin for FY86 originated from the alternative approaches documented in Section 5.1.2.

Table 8-8. Weighted National Averages of Surrogate-Adjusted Concentrations (ng/g) and Standard Errors for Compounds Analyzed in the FY86 NHATS and Also Analyzed in the FY82 and/or FY84 NHATS[1]

Compound[2]	FY82 Weighted Avg.	FY82 (S.E.)	FY84 Weighted Avg.	FY84 (S.E.)	FY86 Weighted Avg.	FY86 (S.E.)
PESTICIDES						
p,p-DDT	203.	(45.)	133.	(18.)	181.	(35.)
o,p-DDT			10.1	(0.3)	4.92	(0.61)
p,p-DDE	1850.	(260.)	1200.	(90.)	2250.	(230.)
o,p-DDE			10.8	(0.7)	6.20	(0.77)
o,p-DDD			97.8	(24.1)	6.09	(0.75)
ALPHA-BHC			15.3	(5.2)	4.96	(0.62)
BETA-BHC	305.	(40.)	196.	(24.)	162.	(13.)
GAMMA-BHC(LINDANE)			14.5	(3.8)	10.2	(3.2)
DELTA-BHC			13.9	(2.8)	5.55	(0.69)
ALDRIN			9.91	(0.24)	5.24	(0.65)
DIELDRIN	182.	(38.)	33.7	(9.8)	48.4	(8.2)
ENDRIN			27.3	(5.4)	63.0	(7.3)
TRANS-NONACHLOR	147.	(36.)	109.	(7.)	126.	(10.)
OXYCHLORDANE			68.9	(5.6)	98.8	(8.1)
HEPTACHLOR EPOXIDE	84.5	(18.5)	71.0	(6.6)	58.3	(3.3)
HEPTACHLOR			14.4	(2.2)	12.2	(6.3)
MIREX	17.2	(2.4)	11.1	(0.9)	10.9	(1.5)
GAMMA-CHLORDANE			9.86	(0.24)	4.88	(0.61)
CHLOROBENZENES						
1,2-DICHLOROBENZENE	19.1	(2.8)			6.97	(0.83)
1,2,3-TRICHLOROBENZENE			22.4	(0.5)	9.73	(1.18)
1,2,4-TRICHLOROBENZENE	13.8	(0.9)	25.0	(1.6)	8.40	(1.02)
1,3,5-TRICHLOROBENZENE			22.4	(0.5)	9.15	(1.11)
1,2,3,4-TETRACHLOROBENZENE			14.9	(0.4)	7.83	(0.97)
1,2,3,5-TETRACHLOROBENZENE			14.9	(0.4)	7.76	(0.96)
1,2,4,5-TETRACHLOROBENZENE			14.9	(0.4)	7.21	(0.89)
PENTACHLOROBENZENE	12.7	(0.6)	15.1	(0.4)	6.83	(0.85)
HEXACHLOROBENZENE	139.	(67.)	41.2	(4.8)	49.9	(3.6)

Table 8-8. (cont.)

Compound[2]	FY82 Weighted Avg.	FY82 (S.E.)	FY84 Weighted Avg.	FY84 (S.E.)	FY86 Weighted Avg.	FY86 (S.E.)
PHTHALATE ESTERS						
DIMETHYL PHTHALATE			14.6	(1.1)	12.9	(1.5)
DIETHYL PHTHALATE	131.	(40.)	12.7	(1.2)	17.0	(2.3)
DI-N-BUTYL PHTHALATE	608.	(168.)	454.	(76.)	58.0	(10.4)
BUTYL BENZYL PHTHALATE	418.	(59.)	149.	(32.)	60.2	(7.3)
BIS (2-ETHYLHEXYL) PHTHALATE			37.0	(6.2)	847.	(356.)
PHOSPHATE TRIESTERS						
TRIBUTYL PHOSPHATE	57.1	(3.5)	10.9	(0.9)	54.7	(6.4)
TRIPHENYL PHOSPHATE	2840.	(2520.)	86.5	(56.3)	29.8	(5.7)
TRIS (2-CHLOROETHYL) PHOSPHATE	50.2	(6.0)	27.3	(5.4)	65.9	(7.7)
TRITOLYL PHOSPHATE			35.2	(5.4)	23.2	(2.7)
PAHs						
NAPHTHALENE	24.3	(3.5)	14.9	(1.4)	20.0	(2.3)
PHENANTHRENE	14.1	(1.3)	32.7	(11.6)	6.08	(0.73)
FLUORANTHENE			11.2	(0.7)	5.58	(0.71)
CHRYSENE			15.8	(2.6)	5.68	(0.69)
ACENAPHTHENE			10.1	(0.3)	5.46	(0.71)
ACENAPHTHALENE			10.1	(0.3)	5.62	(0.73)
FLUORENE			13.0	(2.1)	6.21	(0.81)
PYRENE	11.1	(0.5)	31.9	(18.2)	5.21	(0.68)
PCBs						
MONOCHLOROBIPHENYL			9.95	(0.25)	6.44	(1.07)
DICHLOROBIPHENYL			10.1	(0.3)	6.01	(0.96)
TRICHLOROBIPHENYL	14.6	(1.2)	16.2	(1.0)	13.0	(1.5)
TETRACHLOROBIPHENYL	30.8	(3.5)	50.5	(5.8)	58.3	(4.7)
PENTACHLOROBIPHENYL	134.	(18.)	115.	(13.)	137.	(11.)
HEXACHLOROBIPHENYL	239.	(34.)	204.	(16.)	314.	(19.)

Table 8-8. (cont.)

Compound[2]	FY82 Weighted Avg.	FY82 (S.E.)	FY84 Weighted Avg.	FY84 (S.E.)	FY86 Weighted Avg.	FY86 (S.E.)
PCBs (cont.)						
HEPTACHLOROBIPHENYL	117.	(18.)	140.	(17.)	126.	(13.)
OCTACHLOROBIPHENYL	84.1	(17.2)	19.0	(3.9)	42.9	(5.9)
NONACHLOROBIPHENYL	34.6	(8.7)	21.5	(2.9)	20.6	(2.8)
DECACHLOROBIPHENYL	59.8	(4.8)	24.6	(2.7)	27.5	(3.1)

(1) Weighted averages are the sum of the arithmetic averages of the surrogate-adjusted concentrations within each of the three age groups (0-14 years, 15-44 years, 45+ years), each multiplied by the proportion of the national population in that age group according to the 1980 Census (0.23, 0.46, and 0.31, respectively). Statistics are presented only for those compounds analyzed within a given survey.

(2) Concentrations of p,p-DDE and dieldrin for FY86 originated from the alternative approaches documented in Section 5.1.2.

The findings in this subsection imply that differences between the surveys may not be environmental in nature but may

data results in Table 8-7.

One should remember that no general conclusions on true national concentrations should be made from these tables of descriptive statistics unless results of QC data analysis and statistical modelling agree with the findings.

8.4 STATISTICAL COMPARISON OF NATIONAL CONCENTRATION ESTIMATES

The results from the FY82, FY84, and FY86 NHATS for semivolatiles in composite samples were statistically compared by fitting the additive model (Chapter 6) on data for each survey

separately, calculating marginal estimates and standard errors, and comparing these estimates across surveys through approximate 95% confidence intervals. In order to compensate for differences in recoveries existing across the three surveys, the additive model was fit to the surrogate-adjusted concentrations within each survey (see Section 5.2 on the adjustment method). Previously published results from the FY82 and FY84 NHATS may differ from those presented in this section as the additive model and the adjustment for surrogate recoveries were not previously considered in these surveys. While adjusting for surrogate recoveries attempted to remove effects of differing recoveries across surveys and to better estimate actual sample concentrations, other differences in analytical method and design (documented in Section 8.1) may contribute greatly toward overall differences in the marginal estimates between the surveys.

8.4.1. Semivolatile Compounds Included in Statistical Comparison

Statistical comparisons yield useful conclusions only when sufficient numbers of detectable results are available from each survey. Specifically, statistical analyses were performed on only those compounds detected in at least 50% of the composites within each survey. In addition, comparisons were made only on compounds which were not removed from consideration for statistical analysis in FY86 as a result of the QC data analysis (Section 5.3); thus no phthalates were considered in the statistical comparison. Based on these criteria, the compounds considered for statistical analysis across surveys were the following:

- p,p-DDT
- p,p-DDE
- Beta-BHC
- Trans-nonachlor
- Heptachlor epoxide
- Hexachlorobenzene
- Tetrachlorobiphenyl
- Pentachlorobiphenyl

- Hexachlorobiphenyl
- Heptachlorobiphenyl.

Thus the statistical comparisons were limited to only ten of the most prevalent pesticides, PCB homologs, and chlorobenzenes found in the NHATS over the years.

In addition, the PCB parameters introduced in Section 6.2.1.2 (total PCB concentration, chlorobiphenyl distribution across homologs, and chlorination level) were estimated for FY82, FY84, and FY86 from the estimated average concentration levels for five PCB homologs resulting from fitting the additive model. The additive model was fitted to data for each of these five homologs (tetra- through octa-CB) since these homologs had high detection percentages in FY86. The method for estimating these parameters and their standard errors was documented in Section 6.2.1.2.

8.4.2. Fitting the Additive Model

The method for fitting the additive model, as well as the form of the model itself, was essentially similar between the three surveys. The primary differences in the model fitting approaches across surveys were as follows:

- The FY86 model fitting included an effect for Batches 1-3 versus 4-5 (Section 6.1). This effect was not included in the model for either FY82 or FY84.
- For FY82 and FY84, the errors attributable to measurement error and specimen sampling error were combined into one error term, rather than individually estimated as in the FY86 analysis. An estimate of measurement error was not determined for these two surveys because FY82 QC data were not readily available, and FY84 QC data were not statistically analyzed. Preliminary analyses indicated that measurement error from the FY86 QC data analysis was not appropriate for use in the FY82 or FY84 analyses.

One note should be made in reporting standard errors resulting from the additive model fitting to the FY84 NHATS data. Large absolute error attributable to MSA sampling was observed for p,p-DDE, beta-BHC, pentachlorobiphenyl, and hexachlorobiphenyl in this survey. When this error was included in the formulas for calculating standard errors in the marginal estimates, these standard errors were inflated by two to three orders of magnitude relative to the marginal estimates. Because these errors were likely not an accurate portrayal of the true error, the MSA error was not considered in the additive model fitting in this survey. Thus the calculated standard errors may be somewhat underestimated for these four compounds in FY84.

8.4.2.1. National Estimates. For the above ten semivolatiles and total PCB concentration, Table 8-9 presents the estimated national average concentrations (and standard errors) for each of the three surveys, based on fitting the additive model to surrogate-adjusted concentrations within each survey. This table also contains the estimated overall chlorination percentage for PCBs within each survey. Along with these estimates, Table 8-9 includes the estimated difference from the FY86 estimate for both the FY82 and FY84 surveys and the significance level for testing that this difference differs from zero. The test was based on the approximate t-statistic of the form

$$t = \frac{|NA_{86} - NA_i|}{\sqrt{SE_{86}^2 + SE_i^2}}$$

(i=82, 84), where NA_{82}, NA_{84}, and NH_{86} are the FY82, FY84, and FY86 national average estimates and SE_{82}, SE_{84}, and SE_{86} are their standard errors, respectively. Approximate significance levels were calculated using the standard normal distribution. More exact significance levels based on the Student-t distribution (with degrees of freedom obtained through Satterthwaite's approximation) was deemed too complex to use in this application;

Table 8-9. Comparisons of Predicted National Average Concentrations (ng/g) for Selected Semivolatiles over the FY82, FY84, and FY86 NHATS[1]

	FY82	FY84[2]	FY86	FY86-FY82		FY86-FY84	
Compound	Mean (S.E.)	Mean (S.E.)	Mean (S.E.)	Diff. (S.E.)	p	Diff. (S.E.)	p
P,P-DDT	189. (31.)	123. (11.)	177. (20.)	-12.1 (36.8)	0.74	53.4* (22.4)	0.02
P,P-DDE[3]	1840. (350.)	1150. (90.)	2340. (270.)	498. (441.)	0.26	1190.* (280.)	<0.01
BETA-BHC	291. (54.)	199. (24.)	157. (25.)	-135.* (59.)	0.02	-42.3 (34.7)	0.22
TRANS-NONACHLOR	109. (28.)	105. (5.)	130. (15.)	21.3 (31.5)	0.50	25.8 (16.1)	0.11
HEPTACHLOR EPOXIDE	59.4 (13.4)	68.3 (7.1)	57.6 (4.2)	-1.73 (14.0)	0.90	-10.6 (8.2)	0.20
HEXACHLOROBENZENE	118. (68.)	42.9 (5.4)	51.3 (4.0)	-66.9 (68.2)	0.33	8.38 (6.73)	0.21
TETRACHLOROBIPHENYL	15.7 (1.4)	48.8 (5.9)	56.4 (4.7)	40.7* (4.9)	<0.01	7.60 (7.58)	0.32
PENTACHLOROBIPHENYL	78.3 (7.9)	115. (11.)	135. (15.)	56.2* (17.2)	<0.01	19.8 (18.7)	0.29
HEXACHLOROBIPHENYL	176. (28.)	198. (11.)	314. (18.)	137.* (34.)	<0.01	115.* (21.)	<0.01
HEPTACHLOROBIPHENYL	84.6 (17.0)	129. (10.)	125. (22.)	40.5 (27.7)	0.15	-3.51 (24.2)	0.88
TOTAL PCBS[4]	407. (34.9)	508. (19.5)	672. (34.8)	266.* (49.2)	<0.01	164.* (39.8)	<0.01
CHLOR. LEVEL (%)[5]	59.3 (5.8)	58.1 (2.5)	58.3 (3.5)	-1.0 (6.8)	0.88	0.2 (4.3)	0.96

* Difference is significant at the 0.05 level.

(1) Estimates originate from fitting the additive model on surrogate-adjusted concentrations.
(2) Error due to MSA sampling is not included in the standard error estimates.
(3) m/z = 316 in FY86 NHATS (see Section 5.1.2).
(4) Sum of concentrations for tetra- to octa-chlorobiphenyl.
(5) Overall chlorination level for PCBs, defined in Section 6.2.1.2.

these significance levels are well approximated by the standard normal distribution with the sample sizes observed in each survey.

Significant differences from the FY86 national estimate were observed at the 0.05 level for both the FY82 and FY84 surveys (Table 8-9). In the FY82 survey, the national estimates for the PCB homologs and total PCBs were lower than in the FY86 survey; the difference was highly significant for tetra-, penta-, and hexa-chlorobiphenyls, as well as for total PCBs. However, except for tetrachlorobiphenyl, different IQS were used between the FY82 and FY86 surveys for the PCB homologs. A significant difference in the national estimates for beta-BHC was also observed between FY82 and FY86; the FY86 estimate was 135 ng/g lower than the FY82 estimate. Both surveys used the same IQS for quantitating beta-BHC.

In the FY84 survey, the national estimate for only one of the analyzed PCB homologs differed significantly from the FY86 estimate. The 115 ng/g increase in hexachlorobiphenyl for FY86 relative to FY84 was highly significant. An increase of 164 ng/g in total PCBs for FY86 relative to FY84 was also highly significant. Increases in the FY86 national estimates for p,p-DDT and p,p-DDE relative to the FY84 estimates were also significant at the 0.05 level. All three of these compounds were quantitated using the same IQS in the FY84 and FY86 NHATS.

Table 8-10 presents the estimated chlorobiphenyl distribution across the five prevalent PCB homologs for the FY82, FY84, and FY86 surveys. It is clear that the dominance of hexachlorobiphenyl observed in the FY86 analysis was present in the FY82 and FY84 surveys as well.

8.4.2.2. Marginal Estimates. Marginal estimates for the four census regions, three age groups, two sex groups, and two race groups are presented (with their standard errors) in Tables J-3 through J-6 (Appendix J) for the ten analyzed semivolatiles, total PCBs, and overall chlorination level across the three

Table 8-10. Chlorobiphenyl Distribution Across the Five PCB Homologs Considered for Statistical Analysis in the FY86 NHATS

PCB Homolog	Chlorobiphenyl Distribution[1]		
	FY82 NHATS	FY84 NHATS	FY86 NHATS
Tetrachlorobiphenyl	3.86%	9.60%	8.39%
Pentachlorobiphenyl	19.3%	22.6%	20.0%
Hexachlorobiphenyl	43.4%	39.1%	46.6%
Heptachlorobiphenyl	20.8%	25.3%	18.6%
Octachlorobiphenyl	12.7%	3.46%	6.35%

[1] Chlorobiphenyl distribution for homolog i (i=4,5,6,7,8) is calculated as follows:

$$\frac{\textit{average concentration estimate for Homolog i}}{\textit{average concentration estimate for Total PCB}} * 100\%$$

where "Total PCB" is the sum of the average concentration estimates across the five homologs in the above table. Each homolog omitted from the table was detected in no more than 30% of the NHATS FY86 composite samples.

surveys. The estimates for census regions and age groups are plotted for each survey in Appendix K with plus and minus two standard error bars. The tables also contain estimates of the difference in the marginal estimates between the FY86 survey and each previous survey.

The following results are suggested from the marginal estimates in Tables J-3 through J-6 (references to significant differences between surveys are made at the 0.05 level using the t-test described above):

- Large differences in the estimates of PCB homologs and of total PCB concentration were evident between FY86 and FY82 for many of the subpopulations. These differences, often several times larger than their standard errors, were generally significant for the northcentral and northeast census regions, the 15-44 and 45+ age groups, whites, and both sexes. In each case, the FY86 estimate was higher than the FY82 estimate.

- Among PCB homologs, significant differences in the marginal estimates between FY86 and FY84 were primarily relegated to hexachlorobiphenyl. All subpopulations except the 0-14 age group observed significant differences in the marginal estimate for this homolog between the two surveys. For total PCBs, significant differences between surveys were observed for the northcentral and northeast census regions, the 45+ age group, both race groups, and females. In each case, the FY86 estimate was higher than the FY84 estimate.

- Excluding the PCB homologs, few significant differences in marginal estimates were observed between FY82 and FY86 among the subpopulations.

- Excluding the PCB homologs, there is some evidence that significant differences exist in marginal estimates for p,p-DDT and p,p-DDE between the FY86 and FY84 surveys. Differences in p,p-DDE were significant across all age groups, sex groups, and race groups; the FY86 estimate was larger than the FY84 estimate in each instance. For p,p-DDT, significant differences were observed for the 45+ age group, northeast census region, and males as a result of larger marginal estimates in the FY86 survey.

Thus Tables J-3 through J-6 indicate that whenever significant differences occurred in the marginal estimates between surveys, higher estimates were associated with the FY86 survey. In FY82, most differences occurred with PCBs; these differences were primarily observed for the two highest age groups and the northeast and northcentral census regions. In FY84, most differences were observed for hexachlorobiphenyl, p,p-DDE, and p,p-DDT; these differences tended to be consistent across all subpopulations.

8.4.2.3. Likelihood Ratio Tests. For the ten compounds analyzed within each survey using the additive model, statistical hypothesis tests were conducted within each survey to determine if there were statistically significant differences in average concentration between individuals between different geographic regions, age groups, race groups, and sex groups. Likelihood ratio principles were used to conduct these tests (Section 6.2.2). For the FY86 survey, these tests were performed in Section 7.3.

Table 8-11 lists the significance levels obtained from performing the likelihood ratio tests on the FY82, FY84, and FY86 data. These results show a relative consistency across all surveys. No significant differences were noted across age groups or sex groups in either survey. Significant effects due to census region and age groups were observed in each survey for most of the PCB homologs, hexachlorobenzene, and pesticides. Specifically, the importance of both the census region and age group effects on the concentration values remains evident in the FY86 NHATS as in the prior surveys.

8.4.2.4. Conclusions. The conclusions of statistical analysis on surrogate-adjusted concentrations for semivolatile organic compounds are similar between the three surveys. Age group and census region appear to be the most significant demographic effects on many of these concentrations within each survey.

Table 8-11. Significance Levels from Hypothesis Tests for Differences Between Demographic Groups for Selected Semivolatiles in the FY82, FY84, and FY86 NHATS[1]

Compound[2]	Significance Levels FY82	FY84	FY86
Effect of Census Region			
p,p-DDT	<0.001*	<0.001*	<0.001*
p,p-DDE	0.005*	<0.001*	0.001*
BETA-BHC	0.011*	0.141	0.947
HEPTACHLOR EPOXIDE	0.442	<0.001*	0.031*
TRANS-NONACHLOR	<0.001*	<0.001*	0.187
HEXACHLOROBENZENE	<0.001*	<0.001*	<0.001*
TETRACHLOROBIPHENYL	>0.50	0.216	0.036*
PENTACHLOROBIPHENYL	0.001*	<0.001*	0.009*
HEXACHLOROBIPHENYL	<0.001*	<0.001*	0.047*
HEPTACHLOROBIPHENYL	0.001*	0.408	0.140
Effect of Age Group			
p,p-DDT	>0.50	<0.001*	<0.001*
p,p-DDE	0.001*	>0.50	0.009*
BETA-BHC	0.001*	>0.50	0.015*
HEPTACHLOR EPOXIDE	0.117	<0.001*	<0.001*
TRANS-NONACHLOR	0.022*	<0.001*	<0.001*
HEXACHLOROBENZENE	<0.001*	<0.001*	<0.001*
TETRACHLOROBIPHENYL	0.057	<0.001*	<0.001*
PENTACHLOROBIPHENYL	<0.001*	<0.001*	<0.001*
HEXACHLOROBIPHENYL	0.005*	>0.50	<0.001*
HEPTACHLOROBIPHENYL	0.811	<0.001*	0.001*
Effect of Sex Group			
p,p-DDT	0.952	0.379	0.966
p,p-DDE	0.946	0.694	0.814
BETA-BHC	0.994	0.353	0.623
HEPTACHLOR EPOXIDE	0.534	0.551	0.565
TRANS-NONACHLOR	0.771	0.233	0.321
HEXACHLOROBENZENE	0.974	0.971	0.777
TETRACHLOROBIPHENYL	0.379	0.543	0.260
PENTACHLOROBIPHENYL	0.675	0.617	0.549
HEXACHLOROBIPHENYL	0.562	0.381	0.693
HEPTACHLOROBIPHENYL	0.203	0.243	0.490

Table 8-11. (cont.)

Compound[2]	Significance Levels FY82	FY84	FY86
Effect of Race Group			
p,p-DDT	0.433	0.259	0.286
p,p-DDE	0.805	0.808	0.569
BETA-BHC	0.259	0.452	0.501
HEPTACHLOR EPOXIDE	0.495	0.786	0.846
TRANS-NONACHLOR	0.484	0.711	0.879
HEXACHLOROBENZENE	0.890	0.802	0.936
TETRACHLOROBIPHENYL	0.383	0.908	0.337
PENTACHLOROBIPHENYL	0.605	0.228	0.619
HEXACHLOROBIPHENYL	0.389	0.245	0.244
HEPTACHLOROBIPHENYL	0.280	0.289	0.368

* Significance declared at the 0.05 level.

(1) Data adjusted for surrogate recoveries (see Section 5.2). Likelihood ratio tests are based on the chi-square distribution.

(2) p,p-DDE concentrations for FY86 use m/z=316 (see Section 5.1.2).

Despite the similarities between surveys, differences in estimated subpopulation concentrations were significant for some PCB homologs and pesticides between the FY82/FY84 surveys and the FY86 survey. In most cases, these differences indicated that FY86 estimates were higher than in the previous surveys. These results are contrary to the downward trends concluded in previous trends analyses (Robinson, et. al., 1990). These results are more likely due, however, to analytical effects rather than environmental effects. Since a period of only four years exist between the collection of specimens for these three surveys, it is unlikely that major changes in the actual concentration levels in human adipose tissue will be observed over this time period under normal exposure conditions. In making generalizations across the surveys, such analytical factors as differences in IQS and surrogate compounds between surveys, and differences in design factors, must also be considered as attributable toward observed differences.

The national average estimates from the statistical modelling on ten semivolatiles tend to agree with the estimates obtained from the weighted average calculations (Section 8.3.2). Thus the weighted averages in Table 8-8 may provide useful estimates in national average concentrations which are relatively similar to what would be achieved through statistical modelling.

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16. Abstract (Limit: 200 words)

The Environmental Protection Agency's National Human Adipose Tissue Survey (NHATS) was performed annually to quantify the levels of selected chemicals in the adipose tissue of humans in the U.S. population. Specimens collected in fiscal year 1986 were earmarked for an analysis to estimate national average concentrations of 111 semivolatile compounds in adipose tissue, to identify differences in average concentrations among subpopulations, and to compare results with previous surveys in the NHATS. For 17 semivolatiles detected in at least half of the 50 analytical samples, statistical modeling techniques were conducted to address these objectives.

Among demographic effects on average concentration, the age group effect was most often statistically significant, with higher concentrations associated with higher ages. Among PCB homologs, the 45+ year age group had from 188% to 706% higher average concentrations than the 0-14 year age group, with similar increases observed for pesticides. Geographic effects were only occasionally significant, and no significant race or sex effects were observed.

Statistically significant increases in concentration (generally less than 100%) from the FY82 NHATS were observed for three PCB homologs, while increases of 50% to 100% from the FY84 NHATS were significant for p,p-DDT and p,p-DDE. Mixed findings were observed for other semivolatiles analyzed in all three surveys.

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